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EVALUATION OF PROCESS SYSTEMS FOR EFFECTIVE MANAGEMENT OF ALUMINUM FINISHING WASTEWATERS AND SLUDGES

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16. ABSTRACT

Innovative processes for use in treatment of wastewaters and sludges produced in anodizing, etching and painting extruded aluminum were investigated.

Segregated neutralization of spent caustic etch and spent anodize acids at temperatures of 60 to 90°C and pH values of 5.5 to 10 were examined. Major improvements in thickening and dewatering properties were achieved with increasing values of neutralzation pH while neutralization temperature had minimal impact. Recovery of spent caustic etch by precipitation of aluminum with calcium (i.e., lime) addition was studied. Stoichiometric precipitation of aluminum at temperatures of 25 to 60°C was achieved at Ca/Al ratios of 4 to 5.5 (mass basis). Recovery of aluminum-finishing sludges using sulfuric-acid extraction to produce liquid alum (i.e., $Al_2(SO_4)_3.14 H_2O$) was examined with numerous types of sludges.

Results of the research can be immediately implemented at many aluminum-finishing plants where sludge disposal restrictions and costs are increasing. Segregated neutralization and recovery of spent caustic etch can be used to increase the net solids content of dewatered-sludge available for disposal. Reclamation of dewatered-sludge solids using acid extraction for production of liquid alum has potential for virtual elimination of the need for sludge disposal while producing a net income from this sludge-reclamation process.

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FORWARD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes research undertaken to evaluate the performance of conventional and innovative systems used in the development of treatment strategies to minimize current sludge disposal problems associated with aluminum etching and anodizing processes. Results of this research can be implemented at many aluminum finishing plants where sludge disposal restrictions and costs are increasing.

David G. Stephan
Director
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SECTION 1

INTRODUCTION

Treatment and disposal of wastewaters and sludges produced as a result of cleaning, milling, etching, anodizing and painting aluminum are major problems in the aluminum-finishing industry due to the large quantities and gelatinous properties of sludge solids produced. At many aluminum finishing plants, the mass of wet sludge solid waste approaches the mass of finished aluminum products, representing a major solids disposal problem. Previous research was focused on examination of the characteristics of aluminum-finishing wastes produced in anodizing, etching and painting processes as well as the processes conventionally utilized in treatment of these wastes. Investigations were conducted on techniques to be utilized in improving conventional treatment practices to minimize sludge volume and treatment and disposal costs. The results of the initial portion of the investigation of wastewater treatment practices were presented in a report entitled "Characterization, Reclamation and Final Disposal of Aluminum Bearing Sludges" by Saunders et al. (1982) and submitted to The Aluminum Association Inc. This document served as an initial report on the overall project focused on treatment and disposal of aluminum-finishing wastes and is to be utilized as a major reference source herein.

In this second phase of the overall project, research was focused on examination of innovative treatment processes with potential for achieving major reductions in sludge quantities or reclamation of wastewater or waste metal. The initial focus was placed on an in-depth analysis of waste sources and quantities associated with aluminum etching and anodizing processes using a comprehensive industrial survey. From this survey and from examination of previous experimental investigations (Saunders et al., 1982), three innovative processes were identified for further study.

Spent finishing solutions contain a major portion of the waste aluminum treated at aluminum-finishing plants. Accordingly, a segregated neutralization process was investigated for treatment of concentrated wastes at elevated temperatures to improve sludge handling properties and reduce sludge volume. An innovative etch recovery system was also investigated for use in treating waste aluminum contained in caustic etching solutions. Lime addition to spent etch was examined for removal of aluminum and reclamation of caustic for use in finishing aluminum. Total reclamation of waste aluminum in aluminum-finishing sludges was investigated using direct acidification of sludges with sulfuric acid. The feasibility of production of aluminum sulfate solutions from dewatered sludges was established.

The results of these investigations are presented herein. The initial project report of Saunders et al. (1982) was used as a source document for this study and should be consulted for background information. Sponsors of the research presented herein included the Industrial Environmental Research Laboratory of the U. S. Environmental Protection Agency and the Aluminum Extruders Council. The Aluminum Association Inc., in addition, was a participant in the overall project as presented in the report by Saunders _et al_. (1982) and in this report.

SECTION 2

CONCLUSIONS

The results of the research on innovative treatment processes indicate that they have excellent potential for achieving major reductions in quantities of sludge for disposal and recovery of spent caustic etching solutions as well as economical reclamation of all waste aluminum as a commercially marketable product.

The results of an initial industrial plant survey provided the justification for pursuit of the three innovative processes investigated. From the survey it was concluded that:

1. The majority of waste metal from an anodize line was aluminum removed from alloy surfaces during etching and anodizing with finishing-solution additives providing minor metal loadings. Waste metal quantities in paint-line wastes were significantly lower than those in anodize lines and were equally attributable to aluminum removed from alloy surfaces and chromium discharged from finishing solutions.

2. In anodize lines, rinsewaters contributed the bulk of the wastewater discharged while spent caustic etch, spent anodize acids and dragout from etching tanks were the sources of more than 90 percent of waste aluminum.

3. Water use based on surface area of finished metal was $73.4 m^3/1000 m^2$ and $4.2\ m^3/1000 m^2$ on the anodize and paint lines, respectively. Water use ranged from $27.8\ m^3$/ton to $2.5\ m^3$/ton, based on mass of finished aluminum, for anodize and paint lines, respectively.

4. Dragin rates on an anodize line ranged from 0.092 to $2.87\ m^3/d$ with caustic etch, desmut, anodize and cleaner solutions having rates of from 1 to $2.87\ m^3/d$.

5. With respect to finished aluminum quantities, waste aluminum was discharged at rates of $77.7\ kg/1000 m^2$ and 29.5 kg/ton on the anodize line and was discharged on the paint line at rates of 0.21 $kg/1000 m^2$ and 0.10 kg/ton.

6. The total mass quantity of chromium, cadmium and nickel discharged from an anodize line was less than 0.15 percent of the mass quantity of waste aluminum. The total metal, as the sum of aluminum, chromium,

cadmium and nickel, discharged from a paint line was equal to less than 0.5 percent of the mass quantity of waste aluminum discharged from an anodize line.

Recovery of spent caustic etch by precipitation of aluminum with lime was investigated. From results of these studies, it was concluded that:

1. Removal of aluminum from caustic etch solutions was achieved by precipitation of calcium aluminate using lime addition at reaction temperatures of 25 to 60°C.

2. Reaction kinetics were affected by reaction temperature, reaction time and calcium to aluminum ratio. For a reaction time of six hours, a molar calcium to aluminum dose of 2.75 at 60°C and 3.7 at 25°C was required.

3. Sludge solids produced at calcium to aluminum molar ratios of 1.5 to 3 and temperatures of 25 to 60°C had excellent dewatering characteristics as indicated by specific resistance values of 4.0 to 9.6×10^{10} m/kg.

4. Dewatered sludge solids following aluminum precipitation at molar calcium to aluminum ratios of 1.0 to 3.0 and temperatures of 25 to 60°C ranged from 48 to 53 percent solids.

5. Analysis of the impact of implementation of etch recovery with lime addition at a full-scale anodizing plant indicated a 25 percent reduction in wet sludge mass was achieved as well as a potential chemical saving of $500/day through recovery of spent etching solution.

Segregated neutralization of concentrated finishing solutions was investigated as a means of reducing the volume of sludge solids produced. It was concluded that:

1. Segregated neutralization of concentrated spent etch and acid solutions could be achieved at temperatures of 65 to 90°C in a period of 9 to 10 minutes.

2. Thickening properties of sludges produced were not affected by temperature of neutralization or by 24 hours of aging at ambient temperature.

3. Thickening properties were improved significantly by alkaline neutralization (e.g., pH = 8.5) over neutral or acidic neutralization (e.g., pH = 7.0 and pH = 5.5).

4. Batch flux analysis indicated that thickened sludge concentrations of 4 to 5 percent solids could be routinely achieved in sedimentation basins conventionally used in the industry as compared to conventional-neutralization sludge concentrations of 1 to 2 percent.

5. Dewatering properties of sludges produced by segregated neutralization were improved by use of alkaline pH values of 8.5 and 10.0 as confirmed by specific resistance, CST and filter-leaf yield measurements. Cake solids concentrations from 35 to 54 percent solids were achieved at alkaline pH values indicating a major reduction in final sludge volume.

6. Sludge compressibility coefficients, S_o, were typically below 0.5 and were indicative of highly incompressible sludge solids which was confirmed by improved filter yields with increasing applied vacuum.

7. Evaluation of implementation of segregated neutralization to treat spent finishing solutions at plant A3 indicated that predicted reductions in wet sludge mass ranged from 73 to 80 percent resulting in a major reduction in sludge disposal costs.

8. Segregated neutralizaton of concentrated etch and anodize wastes at alkaline pH and elevated temperatures resulted in formation of a crystalline-like sludge consistent with formation of, for example, pseudoboehmite, gibbsite and bayerite forms as opposed to amorphous non-crystalline aluminum hydroxide.

Direct acidification of dewatered aluminum-finishing sludges for reclamation of waste aluminum as aluminum sulfate solutions was investigated. From this research it was concluded that:

1. Anodize sludge solids produced with conventional and segregated neutralization and aluminum-trihydrate sludges produced from etch-recovery systems reacted rapidly with sulfuric acid to form solutions of aluminum sulfate which meet quality criteria for commercial-grade products.

2. A sludge solids content of 21 percent or higher is required to produce a commercial-strength aluminum sulfate solution with a minimum aluminum concentration of 8.3 percent as Al_2O_3.

3. Aluminum trihydrate sludge produced with etch-recovery systems is best extracted at acid concentrations above stoichiometric requirements to achieve commercial strength. These sludge solids appear to be an excellent feedstock for production of iron-free liquid alum.

4. Direct acidification of aluminum finishing sludges results in solubilization of virtually all sludge solids thereby eliminating sludge disposal requirements for all but a minor residue following alum production.

5. Reclamation of aluminum-finishing sludge as an aluminum sulfate solution is an economical alternative to sludge disposal with an estimated pay-back period of 14 to 21 months.

SECTION 3

RECOMMENDATIONS

The experimental results presented herein provide a strong base for further investigation of innovative treatment processes in the industry. Recommendations regarding the individual processes are presented below followed by those regarding integration of innovative and conventional systems.

Segregated neutralization should be examined in laboratory-and pilot-scale systems to determine the optimal pH and temperature values for treating concentrated etch and anodizing wastes. A comprehensive investigation should be made using a broad range of pH values. Emphasis should be placed evaluating effects on thickening and dewatering properties as well as examination of the fate of waste metals in clarified effluents and dewatered filtrate. Elevated pH values would improve removal of heavy metal contaminants but decrease removal of aluminum. Sludges produced by segregated neutralization can be treated separately but would require redundant systems or multi-phase operation of existing systems. Therefore, the effects of mixing segregated-neutralization suspensions with other conventional wastes should be examined. These neutralized wastes could, for example, be mixed with rinsewaters in a conventional neutralization system, clarifier influent or thickened sludge. The impact of making these mixtures should be investigated.

Lime addition for recovery of spent etch proved to be a successful means of reducing sludge volume and recovering spent etch for reuse in finishing aluminum. The results regarding reaction time, temperature, and lime dose, however, are not sufficient to determine the optimal conditions for installation of such a system. A comprehensive pilot-scale study should be pursued in this regard. In addition, disposal of calcium-aluminate sludge solids which are saturated with a caustic soda solution will be difficult and costly. Research should be conducted to determine if these solids can be washed prior to disposal to remove residual etching solution. Evaluation of a batch-operated perforate-basket centrifuge, similar to that employed in the Fugi Sash etch recovery system (Brown, 1982), should be considered to eliminate the hazardous properties of the sludge due to the presence of caustic soda.

Research on recovery of aluminum-finishing sludges should be conducted to establish the minimum solids content required to achieve commercial-grade standards. In addition, additional aluminum-finishing sludges should be examined to assure the widespread applicability of the process. A comprehensive metal analysis should be included in this program to assure the quality of the alum produced has maximum utility.

Aluminum-trihydrate sludges appear to have excellent potential for production of iron-free alum. Further investigation should be pursued to assure that this product can be consistently used to meet requirements for this high-quality feedstock.

With regard to integration of innovative and conventional treatment systems, it is recommended that a comprehensive pilot-scale system be developed to investigate the concurrent use of etch recovery with lime addition or aluminum-trihydrate formation, segregated neutralization of concentrated finishing wastes and direct acidification of sludges to produce liquid alum with conventional neutralization and sludge treatment processes. The primary objective for such a system would be to establish those process combinations which would provide for maximum reduction in sludge volume and those combinations which result in maximum economical recovery of waste metal and waste finishing solutions.

SECTION 4

BACKGROUND

The research reported herein is the second phase of a project jointly funded by The Aluminum Association Inc., the Aluminum Extruders Council and the Industrial Environmental Research Laboratory of the U. S. Environmental Protection Agency. The results of the initial phase were reported earlier (Saunders _et al_., 1982). The initial report included an extensive literature review of previous research related to treatment and disposal of aluminum-finishing wastes and will not be repeated here. In addition, literature not cited in the earlier report but of importance to the process research reported herein is presented in the initial portions of the appropriate sections.

The earlier report included results of an industrial plant wastewater survey conducted at a participating plant site and the results of an extensive paper-survey conducted by The Aluminum Association, Inc. Research conducted on thickening, dewatering, conditioning,gravity drainage and leaching of conventional wastewaters from five aluminum-finishing plants are reported in the earlier report. These results are extremely important with respect to the information presented herein since they provided the foundation from which many of the reported studies were formulated. The reader is therefore referred to the report by Saunders _et al_. (1982) for detailed background information.

SECTION 5

EXPERIMENTAL METHODS AND PROCEDURES

In conducting investigations of treatment processes for use in the aluminum-finishing industry, it was imperative that wastewaters, sludges and finishing solutions be representative of those encountered in practice. To assure this, waste samples used in the studies reported herein were obtained from aluminum-finishing plants that had participated in the initial portion of this study and as described in detail by Saunders *et al*. (1982).

PARTICIPATING ALUMINUM-FINISHING PLANTS

The reported research was focused on plants using anodizing, etching and painting processes to finish extruded aluminum. Three plants were employed in the research on innovative treatment processes reported herein. Descriptions of these plants are presented in Table 5.1. Plant A1 had separate anodizing and painting lines, in each of which approximately 400 tons of aluminum were finished monthly. This plant served as the site of an intensive industrial waste survey so that relative quantities of wastes generated in anodizing and painting lines could be established.

Plant A2 had an anodize line with a capacity similar to that of plant A1 but did not have a paint line. Waste sludge suspensions collected from this plant were examined with respect to reclamation of waste aluminum as an aluminum sulfate solution. Plant A3 had conventional and integral-color anodizing lines with a monthly capacity of 680 tons of finished aluminum. Waste sludge suspensions and spent etch and anodizing wastes were collected from this facility for use in investigating innovative treatment processes.

Detailed information regarding wastewater quantities and composition and thickening, dewatering and gravity-drainage properties of wastewater suspensions from these plants are presented in an earlier report (Saunders *et al*., 1982). Information on trace metal and priority-pollutant metals and EP-toxicity data are also included in the earlier report.

ANALYTICAL PROCEDURES

Numerous analytical procedures were performed in conducting the research. Chemical characterization was focused on measurement of concentrations of numerous metals while physical characterization included measurements of sludge thickening and dewatering properties. Numerous procedures commonly used throughout the study are presented below while other procedures specific to a particular specific process are presented in later sections.

Table 5.1 Description of Participating Aluminum-Finishing Plants

Plant Designation	Finishing Lines and Production Rates	Wastewater and Sludge Treatment Systems	Sludge Production Rate, kg/mo	
			Wet Basis	Dry Basis
A1	Paint Line: 3.6-4.5x10^5kg/mo.	Paint Line: Two-stage chrome reduction followed by lime neutralization	3.4x10^5 (20% solids)	6.8x10^4
	Anodize Line (clear-coat and integral-color anodize with bright dip and gold dyeing lines): 4.0 - 4.5x10^5 kg/mo.	Anodize Line: Wastewater mixed with lime-neutralized paint-line wastewater; 3-stage pH neutralization, sedimentation, series of lagoons and stream -discharge; sludge: stored in lagoons.		
		Total anodize/paint-line wastewater flow = 1.5x$10^{-2}$$m^3$/s (0.35 mgd). (Anodize-flow to paint-line flow = 7.3)		
A2	Anodize Line (clear-coat anodize w/bright dip and dye lines): 3.6x10^5 kg/mo. or 1.24x10^5 m^2/mo.	pH neutralization; polyelectrolyte flocculation; sedimentation with effluent discharge to surface stream and sludge dewatered on a vacuum filter and landfilled.	1.8x10^5 (20% solids)	3.6x10^4
A3	Anodize Line (including integral-color and clear-coat anodize): 6.8x10^5kg/mo.	3-stage pH neutralization; polyelectrolyte flocculation; sedimentation with effluent discharge to stream; sludge dewatering on 2 filter presses and cake disposal to land on plant site.	1.45x10^6	1.7x10^5

Chemical Analyses

Measurements of pH, alkalinity, acidity, and total, suspended and dissolved solids were conducted in accordance with Standard Methods (1980). Waste samples were prepared for metal analyses by digestion with ultrapure nitric acid (EPA, 1979). Aluminum, calcium, potassium, magnesium, nickel, and iron were determined using a Perkin-Elmer Model 303 atomic absorption spectrophotometer. Lanthanum was added to all calcium solutions at 1 percent to prevent anionic interferences. Standard calibration curves were prepared for use in establishing metal concentrations. Measurements of chromium and cadmium were made using a Perkin-Elmer Model 703 atomic spectrophotometer. A graphite-furnace accessory was used in conjunction with the method of standard addition as presented in detail by Saunders et al. (1982).

Physical Analyses

Thickening measurements were conducted in 1-litre graduated cylinders at suspension heights of 0.4 m. A stirrer located at the wall of the cylinder was rotated at a tip velocity of 0.31 cm/s to minimize wall effects. Tests were initiated by pouring a suspension into a cylinder and mixing the suspension by inverting the cylinder several times. The stirring apparatus was placed in the column and started and interface height was recorded with time.

Dewatering properties of suspensions were established with measurements of capillary suction time (CST), specific resistance and filter-leaf yield. CST is the time required for the liquid portion of a sludge sample to travel 1 cm between two concentric circles on a filter paper by capillary action (Baskerville and Gale, 1968). A type 92/1 CST Apparatus (Triton Electronics Limited) and two hollow, cylindrical, metal reservoirs of 10 mm and 18 mm in diameter were used. The CST filter paper (7 cm x 9 cm) was Whatman 17 chromatography-grade paper.

Specific resistance was measured using the Buchner funnel procedure presented by O'Connor (1975). For a typical test, a 300 ml volume of sludge was filtered under a vacuum of 38 cm Hg (50 kPa) using No. 1 Whatman filter paper placed in a 9-cm diameter Buchner funnel with an effective filtering diameter of 7.5 cm. The volume of filtered liquid was recorded with time and the test was terminated when a crack in the sludge surface caused a sudden drop in vacuum. Filter-leaf measurements are used to obtain design and performance data for vacuum filters and were utilized to measure filter yields. An Eimco filter-leaf apparatus, equipped with NY-319F 3/1 Br Twill multifilament cloth and a filtration area of 92 cm^2, was operated under a vacuum of 6.6×10^4 N/m^2(20 in. of Hg) with a drying time of one minute and a form time of two minutes. The test was performed in accordance with the method described by O'Connor (1975).

SECTION 6

SOURCES OF WASTEWATER CONSTITUENTS

Development and investigation of innovative approaches to reduction or reclamation of aluminum finishing wastewaters and sludges required a detailed examination of the sources of the major wastewater constituents. Since the research program was focused on wastewaters produced in conjunction with etching, anodizing and painting aluminum, plant Al was selected for detailed examination.

PLANT DESCRIPTION

Plant Al had segregated paint and anodize lines with production capacities of 3.6-4.5x10^5 kg/mo and 4.0-4.5x10^5 kg/mo, respectively, as indicated in Table 5.1. The paint line was an automated process used to paint aluminum strips. Pre-painting process steps included: (i) spray wash with an alkaline cleaner; (ii) spray rinse; (iii) conversion-coat formation using a dichromate-fluoride-phosphate process; (iv) spray rinse and (v) acidulating rinse as presented in Table 6.1. The alkaline cleaner and conversion-coat solutions were not discharged to waste. Dragout from these finishing solutions however was carried into the spray rinses which continuously overflowed to a wastewater treatment system.

Table 6.1. Paint Line Process at Plant Al

Tank Number	Finishing Step	Description
PL-1	Spray Wash	Alkaline cleaner, dumped to waste twice a year
PL-2	Rinse	Tap water rinse with continuous overflow to waste
PL-3	Conversion Coat Formation	Solution of Aladine 47 (5.5g/l) and Aladine 407 (58.9g/l)
PL-4	Rinse	Tap water rinse with continuous overflow to waste
PL-5	Acidulating Rinse	Dilute chromic acid (0.4g/l); Discharged to waste on a weekly basis.

The anodize line was a semi-batch system in which racked aluminum extrusions were placed in a series of finishing solutions and rinses. The finishing steps included (i) alkaline detergent cleaner; (ii) acid detergent cleaner; (iii) cold caustic etch; (iv) hot caustic etch; (v) desmut; (vi) bright dip; (vii) integral-color anodize (Duranodic); (viii) conventional sulfuric-acid anodize; and (ix) gold dye as described in Table 6.2. Each finishing step was followed by a single or double counter-current rinse which was discharged continuously to waste, except for the bright-dip rinse waters which were reclaimed and sold.

The integral-color anodize solution was continuously circulated through a cation exchanger at 3.7 l/min to control the accumulation of aluminum. The cation exchange resin was regenerated using 18 percent sulfuric acid when aluminum levels exceeded approximately 1 g/l in the anodize tank. Concentrated regenerant waste was discharged to a storage tank from which it was discharged at a slow rate to the waste treatment system. Concurrent with the discharge of acidic regenerant wastes, plant personnel placed siphons in the caustic etch tanks (AL-5, AL-7) and caustic etch was discharged to the waste treatment system to, in part, neutralize the acidic regenerant prior to discharge to the waste treatment system.

Wastewater treatment at plant Al consisted of (i) a chrome-reduction system to pretreat paint line wastewaters prior to combination with anodize line wastewaters and (ii) a system consisting of neutralization, polymer conditioning and sedimentation used to treat combined anodize-and paint-line wastewaters. These two systems are described in Table 6.3.

Paint-line wastewaters consisted of two continuous rinse overflows while anodize wastewaters consisted of rinsewaters, chemical spills, bright-dip stripping-tower blowdown, acidic ion-exchange regenerant and spent caustic etch. Following chrome reduction of paint-line wastewater, all wastewaters were combined in a four-stage neutralization system to precipitate aluminum as an aluminum hydroxide. Paint-line wastewater was indicated to be approximately 5 to 12 percent of the total wastewater flow with anodize wastewater contributing the remainder.

Following neutralization, precipitated aluminum solids were separated from the wastewater by gravity sedimentation and disposed of in sludge lagoons. Clarified effluent was discharged to two ponds in series with final discharge to a stream.

SURVEY TECHNIQUES

The objective of the survey of the plant was to determine the sources and quantities of Al, Cd, Cr and Ni discharged from each processing line as well as the volume of water discharged. The survey was, furthermore, designed to identify the quantity of each contaminant discharged from each major source.

On the paint line, the two rinsewater overflows discharged to a common channel and segregation of these sources was not possible. On the anodize line, however, all rinsewater overflows were separated and could be sampled. The

Table 6.2. Description of Anodizing Process Line at Plant Al

Tank Number	Finishing Process		Comments
	Description	Contents	
AL-1	Alkaline Cleaner	SC-61 @ 5 g/l; T = 60 to 66°C	
AL-2	Rinse	Tap water rinse with continuous overflow to waste	Rinse for Tank AL-1
AL-3	Acid Cleaner	H_3PO_4 @ 58-65 g/l; Dowanol EB and Triton DF 12 @ 35 g/l; T = 60°C; Air agitation	
AL-4	Rinse	Tap water rinse with continuous overflow to waste	Rinse for Tank AL-3
AL-5	Cold Caustic Etch	NaOH @ 36 g/l, Sorbitol @ 70 g/l; Al^{+3} = 38-60 g/l; T = 43°C; Air agitation	Etch for integral-color anodize. Rinse step performed rapidly to eliminate "run-down"; Approximately 3 m^3/d is siphoned off to neutralize acid from regeneration of ion exchange resin used to remove Al^{+3} from integral-color anodize tank.
AL-6	Rinse	Tap water rinse with continuous overflow to waste	First rinse following hot and cold etch.
AL-7	Hot Caustic Etch	NaOH @ 90-98 g/l, Sorbitol @ 70 g/l, Hailand ND-68E @ 86.4-93.6 g/l; Al^{+3} = 38-60 g/l; T = 60°C; Air agitation	Etch for clear-coat anodize. Approximately 3 m^3/d is siphoned off to neutralize acid from regeneration of resin to remove Al^{+3} from integral-color anodize tank.
AL-8	Rinse	Tap water rinse with continuous overflow to waste	Second rinse following hot and cold etch.
AL-9	Desmut	Nitric acid @ 20 g/l; T = Ambient; Air agitation	

Table 6.2 (continued)

Tank Number	Finishing Process		Comments
	Description	Contents	
AL-10	Rinse	Tap water rinse with continuous overflow to waste	Rinse for tank AL-9
AL-11	Bright Dip	HNO_3 @ 3.2 g/l, H_3PO_4 to achieve specific gravity <1.72; T = 93°C; Air agitation	Rapid transfer (<30 sec) to rinse to minimize air-etch. Dragout is high.
AL-12	Rinse	Batch water rinse	First rinse for bright dip. Tank contents are reclaimed when specific gravity reaches 1.3-1.35 (35% H_3PO_4). Tank contents are reclaimed once every 10 days.
AL-13	Rinse	Batch water rinse	Second rinse for bright dip. Tank contents are transferred to tank AL-12 when dumped, and tap water is used to fill tank AL-13.
AL-14	Storage/Rinse	Tap water rinse with continuous overflow to waste	Used for storage.
AL-15	Transfer Rinse	Tap water rinse with continuous overflow to waste	Used to transfer aluminum from one side of line to other.
AL-16	Storage	Tap water rinse with continuous overflow to waste	Used for storage and as rinse for integral-color anodize.
AL-17	Integral-Color Anodize	D-300 @ 65-85 g/l, H_2SO_4 @ 5 g/l; T = 10 to 21°C	Tank contents vary with shade desired. Tank contents are regenerated with ion-exchange resin to maintain Al $\leq$ 0.9-1.0 g/l.
AL-18&20	Clear Anodize	H_2SO_4 @ 200 g/l; T = 21°C	This acid is used to regenerate ion-exchange resin.
AL-19	Rinse	Tap water rinse with continuous overflow to waste	First rinse for clear anodize tanks AL-18&20.

Table 6.2 (continued)

Tank Number	Finishing Process Description	 Contents	Comments
AL-21	Rinse	Tap water rinse with continuous overflow to waste.	Second rinse for clear anodize tanks AL-18&20.
AL-24*	Seal Rinse	Demineralized water rinse	Continuous recycle of water through demineralizer; Flow ≅ 2.3 m^3/h.
AL-25&26	Seal	Eloxan salt @ 5 gal/tank; pH @ 6.6 (pH adjusted with NaOH and acetic acid); T = 99°C; No mixing	Tank contents dumped to waste on weekends.
AL-27	Dye	Ferric ammonium oxalate @ 14 g/l; pH = 3.8-4.5 (oxalic acid and aqua-ammonia added to adjust pH); T = 99°C	Tank contents are dumped approximately once in 4-6 months. Increasing anodize time increases dye uptake. Time in tank is determined by dye matching.
AL-28	Dye/Cooling rinse	Tap water rinse with continuous overflow to waste.	Used as rinse to cool aluminum after seal tank and dye process.

*Tanks AL-22 and AL-23 were not in use during survey.

Table 6.3. Wastewater Treatment Systems at Plant A2

Treatment Step	Description
Paint Line Wastewater	
Chrome Reduction	Two-stage system to reduce hexavalent chrome to trivalent chrome; Stage 1: H_2SO_4 and SO_2 addition to adjust pH to 2.2 and ORP to 150-175 mw and reduce hexavalent chromium to trivalent chromium. Stage 2: Holding tank for pumping system; Waste pumped to stage 1 of neutralization system and combined with anodize wastewater.
Anodize Line and Paint Line Wastewaters	
Neutralization	Mixed, four-stage system with 4.7 m^3/stage. Stage 1: Wastewaters from paint-line chrome-reduction system and anodize line are combined. Portion of settled sludge is recycled. Stage 2-3: pH is adjusted to within range of 5-8 (Stage 2) and then to pH = 6.2 (Stage 3). Stage 4: Addition of anionic polyelectrolyte and flocculation of precipitated aluminum.
Sedimentation	Continuous-flow, solids-contact clarifier with diameter = 15.3m and depth = 3.7m; Average overflow velocity = 14.5 m/d (355 gpd/sq. ft.) and hydraulic retention time = 3h (i.e., sludge depth of 1.85m).
Polishing Ponds	Clarified effluent is discharged to two ponds in series with final discharge to a stream.
Sludge Lagoons	Underflow from clarifier is discharged to one of four lagoons for ambient-air dewatering. Total available pond volume = 9×10^4 m^3.

survey was conducted for a 24-h period on a Wednesday starting with the third shift of operation. The paint line was operated for two shifts for a total of 16 h while the anodize line was operated continuously during the 24-h survey.

Sampling points were identified in conjunction with plant personnel to collect samples of all wastewaters discharged from the process lines to the wastewater treatment system. Sampling points were also located in the wastewater treatment systems to use to confirm values obtained with samples collected from within the process lines. Samples were collected on an hourly basis for a 24-h period and used to make equal-volume composites for each sample location. Sampling of the cation-exchange system used to remove aluminum from the integral-color anodizing system was conducted during a regeneration cycle at 1-5 min intervals and examined on an individual basis. Also samples of acid regenerant wastewater, as discharged to a holding-tank prior to discharge to the wastewater treatment system, were collected.

RESULTS

Wastewater Flow

Anodize Line--

The flow rates of individual sources of wastewater in the anodize line were set at fixed values prior to the survey and unaltered throughout the 24-hour sampling period where possible. Intermittent wastewater flows, e.g., spent etch and ion-exchange wastewaters, were monitored directly during periods of flow.

Average flow rates for wastewater sources are presented in Table 6.4. Rinse waters constituted the majority (83 percent) of the measured flow from the anodize line. In conjunction with cooling water, backwash water and stripping tower overflow, dilute wastewaters constituted more than 97 percent of the total wastewater flow while concentrated acids (ion-exchange regenerant acid) and bases (spent etch) contained the remainder of the flow.

Paint Line--

The average flow of wastewater from the paint line was 2.71m^3/h for 16 h of operation or 43.3m^3/d. This flow was measured by calibration of the discharge pumps from the chrome reduction system and hourly monitoring of the cumulative time of pumping. The wastewater was pumped to a four-stage neutralization system and combined with anodize wastewater for treatment.

Wastewater Characteristics

To establish wastewater characteristics during the survey, each hourly-sample was analyzed for temperature and pH prior to incorporation into a composite sample. Following transport to the laboratory, composite samples were analyzed for pH and alkalinity, acidity and suspended solids concentrations, which are presented in Table 6.5. Wastewater temperatures did not vary drastically for the anodize line (i.e., 17 to 26°C) with an average rinsewater temperature of 23°C and a measured temperature of 22°C for the combined anodize-line wastewater.

Alkaline cleaner (AL-2), caustic etch (AL-6) and dye/cooling (AL-28) rinsewaters had alkaline pH values and filtrate-alkalinity concentrations of 225, 8742 and 151 mg/l (as $CaCO_3$), respectively. These rinsewaters, furthermore, were

Table 6.4. Wastewater Flow Rate for Anodize Line

Tank Number	Description	Wastewater Flow m^3/d
Rinsewaters		
AL-2	Alkaline Cleaner	29.3
AL-4	Acid Cleaner	18.6
AL-6	Caustic Etch-1	83.5
AL-8	Caustic Etch-2	47.1
AL-10	Desmut	35.5
AL-14	Storage	24.5
AL-15	Transfer	121.5
AL-16	Integral-color anodize	23.6
AL-19	Anodize	21.4
AL-21	Anodize	18.0
AL-28	Dye/Cooling	20.5
	Subtotal	443.5
Other		
-	Bright-dip stripping tower	51.3
-	Pump cooling water	7.5
	Ion exchange	
-	Backwash water	16.3
-	Regenerant acid	9.5
AL-5,-7	Spent Etch	6.3
	Subtotal	90.9
	TOTAL WASTEWATER FLOW	534.4

TABLE 6.5. Wastewater Characteristics for Anodize and Paint Lines

Description		pH**	Composite Temperature* °C	Filtrate Alkalinity mg/l(as $CaCO_3$)	Filtrate Acidity mg/l(as $CaCO_3$)	Suspended Solids mg/l
ANODIZE LINE						
Rinsewaters:						
AL-2	Alkaline Cleaner	7.4	25	225	20	910
AL-4	Acid Cleaner	2.7	23	-	2,584	-
AL-6	Caustic Etch-1	12.0	24	8742	-	1105
AL-8	Caustic Etch-2	2.2	24	-	938	-
AL-10	Desmut	1.8	22	-	5,262	-
AL-14	Storage	3.2	21	-	552	-
AL-15	Transfer	3.5	23	-	333	-
AL-16	Integral Color Anodize	2.8	23	-	1,229	-
AL-19	Anodize	1.3	22	-	18,978	-
AL-21	Anodize	2.4	22	-	1,698	-
AL-28	Dye/Cooling	7.7	26	151	13	942
Others:						
	Bright-dip Stripping Tower	2.6	17	-	1,381	-
	Anodize Wastewater	6.9	22	158	94	3716
PAINT LINE						
	Rinsewater overflow	5.1	31	10	224	955
	Chrome Reduction Effluent	2.3	28	-	802	-

*Average temperature using values of individual samples taken at time of sampling.
**Value measured 4 days after survey.

the only ones which had measurable levels of suspended solids. The remaining rinsewaters and cooling tower overflow wastewater were acidic (pH = 1.3 - 3.5) with acidity values of 333 -18,978 mg/l (as $CaCO_3$). The combined anodize-line wastewater had a near-neutral pH, low levels of acidity and alkalinity and a suspended solids concentration of 3,716 mg/l.

Paint-line wastewater samples were taken at the influent (i.e., rinsewater overflow) and effluent to the chrome reduction system. Paint-line rinsewater was slightly alkaline and had a relatively high temperature of 31°C and a suspended solids concentration of 955 mg/l. As a result of chromate reduction using sulfuric acid, treated effluent from the paint-line system was highly acidic and had no measurable level of suspended solids.

Waste Metals

A major objective of the study, in addition to determination of the sources and quantities of wastewater flow, was to determine the principle sources of waste aluminum, the major component contributing to the production of sludge solids. In addition, since approximately 50 percent of the aluminum finished at the plant was painted following application of a chrome conversion coating, chrome concentrations and mass flows were of interest. Nickel and cadmium concentrations had been shown to be of significance in aluminum-finishing wastewaters (Saunders *et al*., 1982) and, as major toxic contaminants with respect to plants and human and animal health, concentrations and mass flow rates of these metals were to be examined. Therefore, metal analyses were focused on aluminum (Al), chromium (Cr), cadmium (Cd) and nickel (Ni).

Anodize-Line--

Metal concentrations of rinsewaters and other wastewaters discharged from the anodize line are presented in Table 6.6. Ion-exchange regenerant and initial rinses following caustic etch and anodize processes, i.e., tanks AL-6 and Al-19 respectively, contained the highest concentrations of aluminum. Other tanks containing significant concentrations of aluminum included acid cleaner, desmut, second-stage caustic etch (AL-8) and second-stage anodize (AL-21) rinsewaters.

Data presented in Table 6.7 for metal composition of metal-finishing solutions confirm that caustic etch and anodize solutions were principal sources of waste aluminum. The bright dip solution (AL-11) also contained high aluminum levels (51 g/l) as did the two subsequent rinses (22 and 6.54 g/l, respectively). However, no wastewater discharges were made from the tanks since the stage-1 rinse is reclaimed and sold for its phosphorus content. Therefore, only dragout from the stage-2 rinse and vapors trapped in the stripping tower are discharged to the wastewater system from the bright dip process.

The wastewater with the highest concentration of chromium on the anodize line was dragout from the alkaline cleaner (AL-1), as contained in alkaline cleaner rinsewater (AL-2). At a concentration of 475 mg/l, the cleaning solution contained more than approximately 80-fold higher concentration of chromium than any other finishing solution on the anodize line. Other wastewaters with significant levels of chromium included ion exchange regenerant acid and bright-dip-stripping-tower overflow followed by acid-cleaner, desmut and first-stage anodize rinsewaters.

Table 6.6. Metal Composition of Wastewater Sources

Description		Al mg/l	Cr mg/l	Cd μg/l	Ni mg/l
Rinsewaters					
AL-2	Alkaline Cleaner	2.5	17.3	0.37	<0.02
AL-4	Acid Cleaner	325.0	0.6	1.19	<0.02
AL-6	Caustic Etch-1	1,900.0	0.17	0.67	0.22
AL-8	Caustic Etch-2	115.7	2.3	0.36	<0.02
AL-10	Desmut	195.0	0.2	0.23	0.54
AL-14	Storage	37.5	0.013	0.20	<0.02
AL-15	Transfer	16.2	0.014	0.08	<0.02
AL-16	Integral Color Anodize	28.5	0.03	0.48	<0.02
AL-19	Anodize	575	0.126	5.81	0.15
AL-21	Anodize	98.5	0.009	0.53	0.04
AL-24	Seal	1.0	0.005	0.02	<0.02
AL-28	Dye/Cooling	5.33	0.004	0.59	0.03
Other					
-	Bright Dip Stripping Tower	19	0.854	1.7	0.05
	Ion Exchange				
-	backwash-1	18.91	0.0142	0.15	<0.02
-	backwash-2	1.92	0.0126	0.08	<0.02
-	regenerant acid	3,824	0.98	14.4	0.72
	Spent Etch				
AL-5	Cold Etch	47,700	0.63	14,600	1.0
AL-7	Hot Etch	59,600	0.47	29,100	0.4

Table 6.7. Metal Composition of Anodizing Process Solutions

Tank Number	Description	Al g/l	Cr mg/l	Cd mg/l	Ni mg/l
AL-1	Alkaline cleaner	0.059	475.	13.8	0.22
AL-3	Acid cleaner	3.8	4.92	20.2	0.51
AL-5	Cold etch	47.7	0.63	14.6	1.0
AL-7	Hot etch	59.6	0.47	29.1	0.4
AL-9	Desmut	3.2	3.0	6.2	1.0
AL-11	Bright dip	51.0	3.0	4.5	1.25
AL-12	Bright dip rinse-1	22.0	6.0	118.0	2.8
AL-13	Bright dip rinse-2	6.54	6.05	58.2	2.63
AL-17	Integral color anodize	0.75	4.58	91.3	1.20
AL-18	Conventional anodize	5.8	1.42	26.3	0.6
AL-20	Conventional anodize	5.2	0.45	37.8	1.3
AL-25	Seal	0.003	0.004	0.17	<0.02
AL-26	Seal	0.012	0.035	0.37	0.05
AL-27	Dye	0.425	0.34	13.6	0.29

Cadmium concentrations were less than 15 μg/l for all anodize wastewater samples presented in Table 6.6. Nickel concentrations were below detection limits (i.e., 0.02 mg/l) for more than half of the rinsewater samples and less than 0.54 mg/l for the others.

Evaluation of the mass flow of metal was determined with metal concentration data in Tables 6.6 and 6.7 and flow rate data in Table 6.4 and are presented in Table 6.8. The principal source of aluminum was the etching process with a total of 334.64 kg/d of aluminum discharged in spent etch and 164.16 kg/d discharged in caustic etch rinsewaters. The combined flows accounted for 498.8 kg/d, or 88.1 percent of the total of 565.96 kg/d of waste aluminum discharged from the anodize line. The anodize process was the next major source of aluminum with 36.23 kg/d and 13.1 kg/d in ion-exchange regenerant and anodize rinsewaters, respectively. Wastewater discharges resulting directly from anodizing and etching therefore constituted over 96 percent of total waste aluminum from the anodize line.

As reflected by rinsewater concentrations, alkaline cleaner rinsewater was the major source of chromium at 507.47 g/d on the anodize line. Elimination of the use of a chromate-based alkaline cleaner, therefore, would result in a 75.6 percent reduction in the mass flow of chromium. A second major source of chromium appeared to be the second-stage caustic rinsewater (AL-8). However, evaluation of data for chromium content of caustic etch solutions (Table 6.7) and for first-stage caustic rinsewater (AL-6) placed this value in question. All other chromium sources ranged from 0.08 to 14.12 g/d.

Table 6.8. Mass Flow of Metals from Wastewater Sources

Description		Al kg/d	Cr g/d	Cd mg/d	Ni g/d
Rinsewaters:					
AL-2	Alkaline cleaner	0.07	507.47	11	*
AL-4	Acid cleaner	6.05	11.17	22	*
AL-6	Caustic etch-1	158.72	14.12	56	17.96
AL-8	Caustic etch-2	5.44	108.17	17	*
A-10	Desmut	6.93	6.99	8	19.26
AL-14	Storage	0.92	0.31	5	*
AL-15	Transfer	1.97	1.69	9	*
AL-16	Integral Color Anodize	0.67	0.74	11	*
AL-19	Anodize	11.33	2.69	124	3.22
AL-21	Anodize	1.77	0.17	10	0.72
AL-28	Dye	0.11	0.08	12	0.51
	Subtotal	193.98	653.6	285	41.67
Other:					
	Bright Dip Stripping tower	0.98	4.38	87	2.57
	Ion Exchange				
	Backwash	0.13	0.22	2	*
	Regenerant	36.23	9.27	136	6.79
AL-5,-7	Spent Etch	334.64	3.48	134	4.47
	Subtotal	371.98	17.35	359	13.83
	TOTAL	565.96	670.95	644	55.5

*Ni below detection limit of 0.02 mg/l.

Cadmium was discharged in anodize rinsewater (AL-19), ion exchange regenerant and spent etch at 124, 136 and 134 mg/d, respectively, accounting for 61 percent of the total cadmium mass flow. Other major sources included the bright-dip stripping-tower overflow and caustic etch rinsewater (AL-6). Cadmium discharge rates were below 22 mg/d for all other wastewater sources. Nickel discharge totalled 55.5 g/d with caustic etch (AL-6) and desmut (AL-10) rinsewaters being major sources at 17.96 g/d and 19.26 g/d, respectively. Seven of the 16 wastewater sources included in Table 6.8 contained nickel at levels below the detection limit (i.e., 0.02 mg/l) of the procedure used (flame atomic adsorption).

With respect to overall discharge of metals from the anodize line, aluminum discharge was the principal metal at 565.96 kg/d. Mathematical conversion of this mass of aluminum to a precipitated form as aluminum hydroxide ($Al(OH)_3$) would result in prediction of a suspended solids mass flow 1635 kg/d and a suspended solids concentration of 3060 mg/l. The total discharge of chromium, cadmium and nickel equalled 727 g/d or 0.13 percent of the mass of aluminum discharged. These metals, therefore, contributed only a minor portion of the metal to be treated and precipitation of them would only constitute a minor increase in sludge inventories.

Paint-Line--

The flow rate of paint line wastewater was measured using the pumps which transferred paint-line wastewater from the chrome-reduction system to a neutralization system receiving all plant wastewaters. The flow rate averaged 2.7 m^3/h for a period of 16 hours of operation and the total daily discharge of wastewater from the paint-line was 43.3 m^3/d.

Metal concentrations for the wastewater flow and finishing solutions are presented in Table 6.9. Metal concentrations for the paint-line wastewater and chrome reduction effluent were virtually identical since nothing was done in the chrome reduction system to alter the total metal content of the wastewaters and no distinction was made in Table 6.9 between trivalent and hexavalent forms of chromium nor for various forms of the other metals. Chromium and aluminum were the major metals with concentrations between 40 and 47 mg/l. Nickel and cadmium concentrations were much lower at 0.02 - 0.03 mg/l and 0.44 - 0.48 μg/l, respectively.

Table 6.9. Metal Composition of Paint-Line Wastewater and Finishing Solutions

Description	Al mg/l	Cr mg/l	Cd μg/l	Ni mg/l
Wastewater				
Paint-line rinsewaters	40	47	0.48	0.02
Chrome reduction effluent	40.2	43	0.44	0.03
Finishing Solutions				
Alkaline Rinse	168	9.5	0.47	<0.02
Chromate Conversion Coat	<1	5240.0	14.85	0.32
Acidulating Rinse	20	51.5	19.43	<0.02

Examination of the composition of finishing solutions indicated that alkaline rinsewaters and chrome-conversion-coat rinsewaters were, respectively, the major sources of aluminum and chromium. The acidulating rinse solution had the highest cadmium concentration but it was not discharged to wastewater during the survey.

Using a flow rate of 43.3m^3/d and the metal concentration data for the chrome-reduction effluent, metal discharge rates for the plant-line were 1.74 kg/d for aluminum, 1.86 kg/d for chromium, 19.05 mg/d for cadmium and 1.30 g/d for nickel.

Combined Wastewaters--

Combined wastewaters which were sampled included those discharged from the anodize and paint lines and that discharged from the neutralization basin used to treat the combined flow of anodizing and painting wastewaters. Since no samples of individual wastewaters were collected within the paint-line system, metal data were only collected for the combined paint-line wastewater and are presented in Table 6.9. However, numerous sources of wastewater were examined within the anodize line (see Tables 6.6 and 6.8) as well as a composite sample of the combined discharge from the anodize line. Metal data for combined anodize wastewaters are presented in Table 6.10.

Table 6.10. Metal Composition of Anodize and Neutralized Plant Wastewaters

Description	Al mg/l	Cr mg/l	Cd µg/l	Ni mg/l
Combined Anodize Wastewater	850	2.2	0.98	0.08
Neutralization Basin Effluent				
Total	875	6.2	0.97	0.12
Filtrable	7.8	0.32	1.17	0.04
Neutralization Basin Effluent*				
Monday	1000	3.45	1.78	0.1
Tuesday	1420	3.45	3.80	0.1
Wednesday**	1110	6.65	1.60	0.15
Thursday	1500	6.50	2.01	0.23
Friday	770	1.0	1.55	0.15
Average	1182	4.21	2.15	0.15

* Composite samples collected by plant personnel on first shift (2-hour grab samples combined on equal-volume basis for 8-hour period).

** Date on which full 24-hour survey was conducted.

As predicted from characteristics of individual wastewater sources, aluminum was the major metal contained in the combined anodize-line wastewater and the metal data were in general agreement with those presented in Tables 6.6 and 6.8. For example, predicted metal concentrations for the anodize effluent using data in Tables 6.6 and 6.8 were Al = 1059 mg/l, Cr = 1.3 mg/l, Cd = 1.21 µg/l and Ni = 0.104 mg/l. Predicted aluminum levels were higher than measured aluminum by 20 percent. This error was attributable to the discharge of the bulk (i.e., 59 percent) of the waste aluminum as spent etch (see Table 6.8) during the first shift with no adjustment in composite-sampling frequency due to this flow.

Data for the neutralization basin effluent in Table 6.10 reflect the combined metal flows of anodize- and paint-line wastewaters. Using data in Tables 6.4,6.8 and 6.9, predicted metal concentrations were: Al = 983 mg/l; Cr = 1.17 mg/l; Cd = 1.15 μg/l and Ni = 0.098 mg/l. The predicted and measured data were in excellent agreement, considering the low levels of several metals and the unsteady discharge of some wastewaters. Filtrable metal data indicated that aluminum, chromium and nickel were effectively precipitated with dissolved residuals of 7.8 mg/l, 0.32 mg/l and 0.04 mg/l, respectively. Cadmium precipitation did not occur due, most probably, to the extremely low levels (≈1 μg/l) of the metal in the wastewater.

To relate the results of the survey to other days of operation, plant personnal developed 8-hour composite samples (i.e., grab samples taken at 2-hour intervals during the first shift) for testing during the first shift for five days. Results of metal analyses for these samples are presented in Table 6.10. Since spent etch was routinely discharged during this shift and since the paint line was operational during this shift (but only 16 hours of the 24-hour survey) metal concentrations, especially aluminum, were expected to be slightly higher than those of the 24-hour composite sample. This was the case but the samples collected during the week of the survey were in general agreement with the samples collected during the survey.

Aluminum Production

Production records for the week of the study were collected and examined with respect to survey results. Aluminum alloys processed during the week of the survey were 6063 and 6463 (see Table 6.13) with the majority of the metal being 6063, i.e., 86.3 percent of the total surface area finished for the day of the survey. Production data for the plant are presented in Table 6.11 for the week of the survey. The data presented for the 24-hour period of the survey (i.e., Wednesday) included data from the third shift of Tuesday and the first and second shifts of Wednesday and are, therefore, not consistent with the values recorded for the 24-hour period of the survey.

The quantities of aluminum finished on the anodize- and paint-lines were approximately equal with the material painted having a higher surface area per unit mass, i.e., 0.48 m^2/kg vs 0.38 m^2/kg. Total production was 36.8 T/d or 1.57 x 10^4 m^2/d and was indicative of monthly production rates of approximately 736 T/mo or 3.14 x 10^5 m^2/mo (i.e., for 20 day/mo), which were slightly below indicated production capacities. Production on the anodize line during the survey was consistent with production levels throughout the survey week, which averaged 18.9 T/d and 8.14 x 10^3 m^2/d. Paint-line production during the survey week was reduced to that for one hour of operation on Thursday and no production on Friday due to a mechanical breakdown. However, production on the day of the survey was near the average levels of production for the three days of full operation for the survey week (i.e., 15.8 T/d and 8.6 x 10^3 m^2/d).

Table 6.11. Aluminum Production Data for Plant A1

Description	Finished Aluminum Length 10^3m	Surface Area 10^3 m^2	Mass Ton	Area/Mass m^2/kg
Survey Day				
Anodize Line	32.6	7.3	19.2	0.38
Paint Line	30.0	8.4	17.6	0.48
Week of Survey				
Anodize Line:				
Monday	38.5	8.7	18.2	0.48
Tuesday	41.3	10.7	23.5	0.46
Wednesday	30.2	6.7	17.2	0.39
Thursday	31.8	7.7	18.0	0.43
Friday	30.7	6.9	17.7	0.39
Paint Line:				
Monday	38.2	9.7	16.4	0.59
Tuesday	63.9	7.8	13.4	0.48
Wednesday	30.0	8.4	17.6	0.48
Thursday	2.3	0.8	1.8	0.44
Friday	0	0	0	-

With respect to the specific finishing operations utilized, the paint line was an automated system and all aluminum was finished using the same identical processes. However, several finishing sequences were utilized on the anodize line resulting in variations in use of the available finishing processes as included in Table 6.2. The portions of aluminum which were finished during the survey using the various processes are included in Table 6.12. The hot etch process was not used during the survey and the cold etch and bright dip processes were only used on 70.5 - 72.8 percent and 29.5 - 27.2 percent of the aluminum finished, respectively. All aluminum was anodized (conventional clear-coat sulfuric-acid anodize = 80-86 percent and integral-color sulfuric-acid anodize = 14-20 percent) and all other processes were used in finishing the aluminum processed during the survey.

Table 6.12. Anodizing Processes Utilized during the Survey Period

Tank Number	Description	Percent of Total Finished		Cumulative time of treatment hour
		Surface Area	Mass	
AL-1	Alkaline Cleaner	100	100	10.5
AL-3	Acid Cleaner	100	100	*
AL-5	Cold Etch	70.5	72.8	21.6
AL-9	Desmut	100	100	3
AL-11	Bright Dip	29.5	27.2	1.2
AL-17	Integral-Color Anodize	14.4	19.7	24
AL-18&20	Clear Anodize	85.6	80.3	31.5
AL-24	Seal Rinse	100	100	0.75
AL-25&26	Seal	100	100	30
AL-28	Dye/Cooling Rinse	100	100	0.75

*time not available

DISCUSSION

Sources of Waste Metals

Waste metals at Plant A1 were either additives in the finishing solutions or constituents of the alloys being finished. The alloys finished during the study were similar in composition as indicated in Table 6.13. The alloys typically contain no nickel or cadmium, although cadmium would be expected to be a low-level contaminant of zinc added to 6063. Chromium is contained in 6063 at a maximum of 0.1 percent or $\leq$ 1,000 mg Cr/kg Al.

Table 6.13. Chemical Composition Limits of Wrought Aluminum Alloys (Aluminum Association, 1979)

Alloy	Metal Content Percent of Alloy Mass*									
	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others	Al
6063	0.2-0.6	0.35	0.1	0.1	0.45-0.9	0.1	0.1	0.1	0.05-0.15	Remainder
	(0.4)	-	-	-	(0.67)	-	-	-	-	"
6463	0.2-0.6	0.15	0.2	0.05	0.45-0.9	-	-	-	0.05-0.15	Remainder
	(0.4)	-	-	-	(0.7)	-	-	-	-	"

*Values in brackets are nominal composition limits.

Anodize Line--

Since etching and anodizing result in the removal of surface metal during finishing, the levels of cadmium, chromium and nickel removed from alloy surfaces would be small in comparison to the quantity of aluminum removed. Addition of cadmium, chromium and nickel to finishing solutions would result in higher levels of these metals in a finishing solution, relative to aluminum, and would not be proportional to aluminum removal rates. To determine the sources of metals examined, the composition of rinsewaters and finishing solutions were expressed with respect to aluminum concentrations and are presented in Table 6.14 for the anodize line. With respect to chromium, alkaline cleaner was the principal source with levels of 6.92 kg Cr/kg Al, since chromium was an additive in the process tank. The acid cleaner, with a chromium level of 1.85 g/kg, may also have contained a low level of chromium-based cleaner. However, all other rinsewaters contained chromium at levels indicative of those attributable to chromium removal from alloys.

Cadmium composition of acid cleaner rinsewater was equal to 3.66g/kg but this value was not confirmed by the 5.3 mg/kg value for the acid cleaner finishing solution. All other sources were $\leq$ 353 mg/kg with the majority being $\leq$ 20 mg/kg, indicating maximum alloy composition levels of 0.035 percent and 0.002 percent, respectively (assuming Cd levels were attributable to alloy impurities). Cadmium levels in this range, i.e., 0.002 to 0.035 percent, are reasonable with respect to alloy content. Removal of cadmium from alloys being finished was the apparent source of cadmium.

Table 6.14. Relative Trace Metal Composition of Anodizing Rinsewaters and Finishing Solution

Description		Cr/Al mg/kg	Cd/Al mg/kg	Ni/Al mg/kg
Rinsewaters				
AL-2	Alkaline Cleaner	6,920,000	148	8,000
AL-4	Acid Cleaner	1,850	3,660	61.5
AL-6	Caustic Etch-1	89.5	353	116
AL-8	Caustic Etch-2	(19,900)	3.1	173
AL-10	Desmut	1,030	1.2	2,770
AL-14	Storage	347	5.3	533
AL-15	Transfer	864	4.9	1,230
AL-16	Integral Color Anodize	1,053	16.8	702
AL-19	Conventional Anodize	219	10.0	260
AL-21	Conventional Anodize	91	5.4	406
AL-28	Dye/Cooling	750	111	5,630
Finishing Solutions				
AL-1	Alkaline Cleaner	8,050,000	234	3,700
AL-3	Acid Cleaner	1,295	5.3	134
AL-5	Cold Etch	13.2	0.3	21
AL-7	Hot Etch	7.9	0.5	6.7
AL-9	Desmut	938	1.9	313
AL-11	Bright Dip	59	0.009	24.5
AL-12	Bright Dip Rinse-1	272	5.4	127.
AL-13	Bright Dip Rinse-2	925	8.9	402
AL-17	Integral Color Anodize	6,110	122	1,600
AL-18	Conventional Anodize	245	4.5	103
AL-20	Conventional Anodize	87	7.3	250
AL-25	Seal	1,330	56.7	<6,700
AL-25	Seal	8,750	92.5	12,500
AL-27	Dye	3,200	128.	2.730

Nickel content of alkaline cleaner, desmut and dye/cooling rinsewaters ranged from 2770 to 8000 mg/kg. Since nickel was not an alloy additive, it is apparent that nickel was a chemical additive in the associated finishing solutions. Nickel levels in the sealing solutions (AL-25 & 26) were attributable to nickel additives (eloxal salt) used to assure proper sealing of anodized surfaces. Nickel contained in the alkaline cleaner solution was apparently a contaminant associated with the chromate additive. Data for the nickel content of the desmut solution did not confirm desmut rinsewater as a major source of nickel additives. Other sources of nickel ranged from 61.5 to 1230 mg/kg which, if attributable to alloy composition, indicated nickel levels in the alloys of 0.006 percent to 0.12 percent. These levels appeared to be relatively high for alloys with no required nickel additives but alloy contaminants could have contributed to the nickel loadings.

In summary, with the exception of chromium and nickel additives in the alkaline cleaner and nickel additives in the sealing solutions, removal of cadmium, chromium and nickel concurrently with aluminum from alloy surfaces was the major means by which these metals entered wastewaters. Therefore, metal contamination is inherent to etching and anodizing processes and with the exception of additives to the alkaline cleaner and sealing solutions, can only be controlled with changes in alloy composition or finishing procedures.

Paint Line--

Paint-line wastewaters included rinsewater discharges following alkaline cleaner and chromate-conversion solutions. These rinsewaters could not be separated for sampling and were sampled collectively as one discharge. Metal composition data for paint-line rinsewater and finishing solutions are presented in Table 6.15. Chromium was obviously the major metal discharged from the paint line and its presence was due to dragin from the alkaline cleaner and chromate conversion solutions. Cadmium and nickel discharges were furthermore significantly affected by composition of the chromate-conversion solution. Metal discharges from the paint-line were, therefore, due primarily to dragin of additives contained in finishing solutions as opposed to removal of metal from aluminum surfaces during finishing.

Table 6.15. Relative Trace Metal Composition of Painting Rinsewaters and Finishing Solutions

Description	Cr/Al mg/kg	Cd/Al mg/kg	Ni/Al mg/kg
Paintline Rinsewater*	1.18×10^6	12	500
Finishing Solutions:			
Alkaline Cleaner	5.65×10^4	2.8	<119
Chromate Conversion	5.24×10^9	1.49×10^4	$>3.2 \times 10^3$
Acidulating Rinse	2.68×10^6	970	$<1 \times 10^3$

*Combined discharge of alkaline-cleaner rinsewater and chromate-conversion rinsewater.

Dragin Rates

Although concentrated finishing solutions were major sources of wastewater contaminants, the major source of wastewater was rinsewater. Using data for flow and metal composition of rinsewaters and finishing solutions, it was possible to determine dragin flows, Q_D, for each finishing tank according to the formula $Q_D = Q_R C_R C_D^{-1}$, where Q_R = rinsewater flow; C_R = contaminant concentration in rinsewater; and C_D = contaminant concentration in dragin (i.e., concentration in preceeding tank).

Anodize Line--

Dragin values are presented in Table 6.16 for anodize-line rinsewaters. Dragin values based on nickel were not calculated due to limited data for rinsewater nickel concentrations. With the exception of three abnormally high values and one low value, dragin flow rates ranged from 0.053 m^3/d to 3.08 m^3/d. As expected, viscous finishing solutions resulted in the highest dragin rates. Caustic etch (AL-6 & 8), anodize (AL-19 & 21), desmut (AL-10) and acid cleaner (AL-4) rinsewaters had dragin rates ranging from 2.87 to 1.38 m^3/d (based on average values). A low dragin rate of 0.34 m^3/d for the integral-color anodize system was attributed to low usage of this solution during the survey. The lowest dragin rate was for the dye/cooling rinse which was due to the decreased viscosity of the high-temperature sealing solution.

Table 6.16. Dragin Rate for Anodize-Line Rinsewaters

		Q_D, Dragin m^3/d			
Tank Number	Description	Al	Cr	Cd	Average
AL-2	Alkaline Cleaner	1.24	1.07	0.79	1.03
AL-4	Acid Cleaner	1.59	2.27	1.10	1.65
AL-6	Caustic Etch-1	1.48	(12.8)*	1.28	1.38
AL-8	Caustic Etch-2	2.87	**	(25.3)*	2.87
AL-10	Desmut	2.16	2.37	1.32	1.95
AL-14	Storage	0.14	0.053	0.084	0.092
AL-16	Integral Color Anodize	0.90	0.0015	0.12	0.34
AL-19	Conventional Anodize	1.12	1.44	1.94	1.62
AL-21	Conventional Anodize	3.08	1.29	1.64	2.00
AL-28	Dye/Cool	0.26	0.24	0.89	0.46

*High values excluded from indicated averages.
**Calculated dragin flow was greater than rinsewater flow.

Paint Line--

Examination of dragin rates for individual rinsewaters was not possible since flow rates for the individual rinsewaters were not collected. However, examination of chemical composition data in Tables 6.9 and 6.15 indicated that the total rinsewater discharge had a chemical composition which was intermediate between the alkaline cleaner and chromate-conversion solutions. Although tap water was added to the rinsewater tanks, if it was assumed that no tap water addition occurred, the dragin rate for the alkaline cleaner solution would account for more than 99 percent of the rinsewater flow. However, it was not possible to confirm this since the relative flows of rinsewater were unknown and dragin rates could not be calculated.

Wastewater Summary

The major source of wastewater and waste metal at plant A1 was the anodize line. As shown in the data summary in Table 6.17, the majority (i.e., 94 percent) of the wastewater from the anodize line was contained in dilute rinsewater with concentrated acids and alkali containing the remainder. Therefore, efforts to reduce water use should be focused on minimizing rinsewater flow by, for example, use of extensive countercurrent rinsing and reuse of treated wastewater effluent for rinses following cleaning and etching.

Table 6.17. Summary of Wastewater and Metal Flows for Anodizing Line at Plant A1

Description	Wastewater Flow	Metal Flow			
	m^3/d	Al kg/d	Cr g/d	Cd mg/d	Ni g/d
Rinsewaters	502.3	195.0	658.0	372	44.2
Ion Exchange Wastewater	25.8	36.4	9.5	138	6.8
Spent Etch	6.3	334.6	3.5	134	4.5
TOTAL	534.4	566.0	671.0	644	55.5
Average Metal Concentration		1059mg/l	1.26mg/l	1.2μg/l	0.104mg/l

With respect to waste metal, aluminum accounted for the majority, i.e., 99.9 percent, of the total of the four metals monitored and therefore accounted for the majority of the suspended solids treated at the plant. However, unlike the wastewater flow, the major sources of waste aluminum were spent etch and ion exchange regenerant, which were minor sources of wastewater. Reduction in the mass flow of aluminum should therefore be focused on reducing the quantity of spent etch and the concentration of aluminum in etch. Reduction of aluminum concentration in spent etch would furthermore reduce alumimum mass flows for etch rinsewaters. The mass flows of chromium, cadmium and nickel were very low as indicated by average wastewater concentrations of 1.26 mg/l, 1.2 μg/l and 0.104 mg/l, respectively, and as compared to 105 mg/l for aluminum.

As discussed earlier, the paint-line system was automated and was operated to minimize wastewater flows. Total wastewater flow was $43.3m^3$/d (for 16 hours of operation) while metal flow rates were 1.74 kg/d, 1.86 kg/d, 19.05 mg/d, and 1.3 g/d, respectively, for aluminum, chromium, cadmium and nickel. These levels were significantly less than those for the anodize line, except for chromium. The use of a chromate-based conversion-coat process resulted in a chromium mass flow which was more than 2.7 times higher than that for the anodize line. The overall mass flow of metals examined was 3.6 kg/d which was 0.64 percent of that for the anodize line.

An analysis of wastewater flows with respect to finished metal is presented in Table 6.18. With the exception of chromium, the anodize line had the highest waste-metal flow rate, as well as the highest wastewater flow rate. In addition, waste aluminum from the anodize line totalled 2.95 percent of aluminum produced, on a mass basis, while that from the paint line totalled 0.01 percent. Anodizing processes therefore include more aggressive finishing steps resulting in the removal of considerably more surface metal and the consequent production of increased quantities of precipitated metals for disposal.

Table 6.18. Wastewater and Metal Flows Normalized to Production of Finished Metal

Wastewater Constituent	Surface Area of Finished Metal		Mass of Finished Metal	
	Anodize Line	Paint Line	Anodize Line	Paint Line
Flow	73.4 $m^3/1000m^2$	4.2 $m^3/1000m^2$	27.8 m^3/ton*	2.5 m^3/ton*
Al	77.7 $kg/1000m^2$	0.21 $kg/1000m^2$	29.5 kg/ton	0.10 kg/ton
Cr	91.9 $g/1000m^2$	221 $g/1000m^2$	34.9 g/ton	105.7 g/ton
Cd	0.088 $g/1000m^2$	0.0023 $g/1000m^2$	0.03 g/ton	0.001 g/ton
Ni	7.6 $g/1000m^2$	0.9 $g/1000m^2$	2.9 g/ton	0.074 g/ton

*metric ton (1000 kg)

Note: $1m^3/1000m^2$ = 24.5 gal/1000 ft^2

$1m^3$/ton = 0.12 gal/lb

The total wastewater flow during the survey period was estimated to be 577.7 m^3/d from anodize- and paint-line flows. This value was equal to 97.13 percent of the measured water flow used in the two lines and was therefore considered to be satisfactory. The suspended solids concentration of the combined effluent from the neutralization basin was 3387 mg/l which was then indicative of a suspended solids mass flow of 1956.7 kg/d. Examination of this value with respect to sludge production was not possible since sludge was not mechanically dewatered at the plant but was periodically pumped to sludge lagoons. However, from data in Table 6.10, the aluminum content of the sludge solids were estimated to be 0.258 g Al/gSS, which was within the range of 0.206 to 0.381 g Al/gSS presented by Saunders et al. (1982) for aluminum finishing sludges. Although inert suspended solids concentration was not determined, using a typical ratio of inert suspended solids to total suspended solids of 0.75, the aluminum content of sludge solids was 0.344 g Al/gISS (ISS = inert suspended solids). This latter value was in excellent agreement with a theoretical value for aluminum hydroxide of 0.346 g Al/g $Al(OH)_3$ indicating it to be the major sludge precipitate. The sludge produced from the facility was therefore typical of other aluminum-finishing sludges examined earlier (Saunders *et al.*, 1982) and was considered to be typical of those produced by anodizing plants. In addition, research conducted by Kratz (1981) indicated that sludges produced from paint-line wastewaters had thickening properties similar to those produced in anodizing plants.

With respect to finished-metal production rates, suspended solids production rates were 124.6 kg/1000m^2 and 53.17 kg/ton. If dewatered sludge was assumed to be 16 percent solids, wet sludge production rates were estimated to be 778.9 kg/1000m^2 and 332.3 kg/ton. Dewatered sludge production therefore was estimated to be equal to 33.2 percent of the total mass of finished aluminum products. Considering that the paint-line wastewater contained only 0.3 percent ((1.74 kg/d)/(567.7 kg/d)) of the total aluminum discharged, the dewatered sludge production was estimated to be 1675 kg/1000m^2 and 636.9 kg/ton. Therefore, the estimated quantity of wet dewatered sludge was 63.69 percent of anodized metal, indicating the magnitude of the sludge disposal problem associated with anodizing processes.

SECTION 7

SEGREGATED NEUTRALIZATION OF CONCENTRATED ALUMINUM-FINISHING WASTES

As indicated in section 6 and by Saunders, et al. (1982), concentrated finishing solutions and wastewaters contain a major portion of waste aluminum produced in aluminum etching and anodizing plants. These wastes include spent etch, spent anodizing acids and ion-exchange regenerants (integral-color anodizing). Initial results presented by Ledfore (1955) and Fukuyama et al. (1974) indicated that neutralization of concentrated finishing solutions on a batch basis resulted in formation of sludges with increased crystalline structure. These sludges, furthermore, were indicated to have improved thickening and dewatering properties. In addition, information presented by Saunders et al. (1982) indicated improved thickening and dewatering properties were achieved with sludge suspensions produced by periodic treatment of concentrated aluminum-finishing wastes at high temperature, i.e., that produced from heat of neutralization, at a full-scale anodizing plant. The sludge produced through neutralization of concentrated etch and acidic anodize wastes had thickening properties which were better than those of the conventional aluminum-finishing sludge examined and could be dewatered to a final solids content which was approximately twice that achieved with conventional aluminum-finishing sludges.

From these published results, it was apparent that neutralization of spent, concentrated finishing solutions at aluminum-finishing plants could have benefical impact on sludge treatment and disposal practices. Since temperature and pH of neutralization were principle variables, they were examined with respect to impact on sludge thickening and dewatering properties. Since heating of spent wastes prior to treatment was to be avoided and since an elevated suspension temperature was critical, the heat generated by neutralization of concentrated acid and alkali was to be used as the sole source of heat. To do this, the acidic and alkaline wastes were not to be diluted and concurrently neutralized with large volumes of rinsewaters but were to be segregated from all other waste so as to allow for the development of elevated temperatures. Hence "segregated" neutralization of concentrated finishing wastes was pursued to determine the effects of pH and temperature on sludge characteristics. Since the primary objective of the research project was to investigate processes for use in reduction in or reclamation of waste sludges, the study was focused on thickening and dewatering of sludges provided by segregated neutralization.

EXPERIMENTAL REACTOR SYSTEM

Investigation of segregated neutralization of concentrated aluminum-finishing wastes was conducted in a continuous-flow, laboratory-scale reactor system shown schematically in Figure 7.1. A double-walled glass reactor was used as the neutralization basin. An external cooling system was used to control temperature by circulation of coolant through an outer jacket of the reactor. The reactor was stirred with a single flat-blade paddle and pH was monitored and controlled with an automatic pH-controller system. Alkaline etch and acidic anodize solutions were pumped into the reactor using peristaltic pumps. The flow rate for the alkaline etch solution was set at a constant value while the flow rate of the acidic anodize solution was regulated by a pH-controller system to maintain a set pH value. Individual flow rates were set prior to each experimental run based on a batch titration run such that the total flow rate was equal to approximately 76ml/min. With a reactor volume of 0.7 litre, the retention time in the reactor was approximately 8-10 min.

Neutralized contents were continuously removed through a vacuum line to a storage vessel which was maintained at the temperature of the neutralized suspension. The reactor was operated for approximately 4 hours to collect 18 litres of neutralized suspension. Following completion of an experimental run, the suspension was concentrated by gravity and immediately examined and, then, gravity settled for a 24-hour period and examined again.

Samples of alkaline etch and acidic anodize solutions were collected immediately prior to each experimental run from plant A3. These solutions were maintained in separate, mixed reservoirs at room temperature and pumped into the neutralization vessel at controlled rates. Characteristics of the wastes varied with each experimental run, however, data presented in Table 7.1 indicate ranges of values for the characteristics of the wastes used.

Experimental studies were conducted in two phases with emphasis in phase 1 placed on determination of process feasibility and examination of the effects of temperature and pH on sludge thickening properties. Phase 2 was focused on a detailed evaluation of sludge dewatering properties and the associated effects of pH.

Table 7.1. Range of Characteristics of Spent Anodize and Etch Wastes from Plant A3

Parameter	Sulfuric-Acid Anodize Solution	Alkaline Etch Solution
Temperature*, °C	21-25	50-60
Aluminum, g/l	7.5-15	35.6-65
Alkalinity, g/l (as $CaCO_3$)	-	275-520
Acidity	340-400	-
pH	0.3-0.6	13.3-13.8
Color	light brown	blue-green

*Temperature of solution at time of collection.

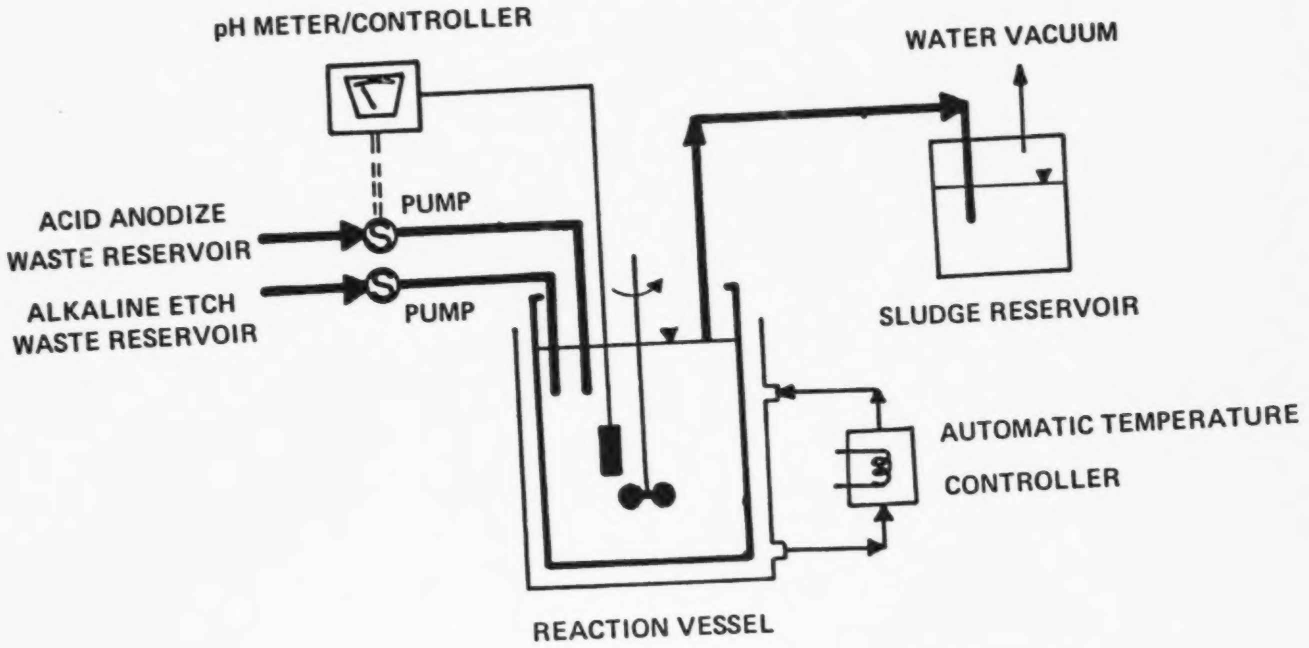
pH METER/CONTROLLER
WATER VACUUM
PUMP
ACID ANODIZE WASTE RESERVOIR
ALKALINE ETCH WASTE RESERVOIR
PUMP
SLUDGE RESERVOIR
AUTOMATIC TEMPERATURE CONTROLLER
REACTION VESSEL

Figure 7.1. Schematic Diagram of Laboratory-Scale Reactor System used for Segregated Neutralization Studies.

PHASE 1 - THICKENING

Experimental Techniques

Anodize and etch solutions obtained from plant A3 had characteristics as presented in Table 7.2. Initial studies conducted with these solutions produced highly viscous suspensions which were difficult to mix and collect. Subsequent studies were therefore conducted with one-tenth dilutions of the solutions in Table 7.2.

Table 7.2. Characteristics of Waste Solutions Used in Phase 1

Parameter	Sulfuric-Acid Anodize Solution	Spent Etch Solution
Temperature*, °C	25	60
Aluminum, g/l	15	65
Alkalinity, g/l (as $CaCO_3$)	-	275
Acidity, g/l (as $CaCO_3$)	400	-
pH	0.3	13.3
Color	light brown	blue-green

*Temperature at time of sampling.

Neutralized suspensions were collected at or near the temperature of neutralization and analyzed immediately following collection. Interfacial settling velocities were determined using stirred (0.3 cm/s), 1-litre graduated cylinders (internal diameter = 6 cm, initial sludge height = 0.4 m) over a range of suspended solids concentrations. A total of five experimental runs were made, as summarized in Table 7.3.

Table 7.3. Experimental Conditions During Runs in Phase 1

Parameter	Experimental Run				
	1	2	3	4	5
Neutralization pH	7.1	7.0	7.3	5.5	8.5
Neutralization Temperature, °C .	65	80	90	80	80
Settling Analysis Temperature,°C					
Initial	48	80	72	80	80
After 24-hour storage . . .	22	23	24	23	23
Waste Flow Rate					
Anodize Acid, ml/min	36	36	36	37.5	41.5
Spent Etch, ml/min	40	40	40	38.5	34.5

Experimental Results

Two groups of experiments were conducted to determine the effects of temperature and the effects of neutralization pH on sludge thickening properties.

Effects of Neutralization Temperature--

Since etch and anodize solutions are typically maintained at temperatures of 50 to 60°C and 21 to 25°C, respectively, and since the heat released during neutralization of concentrated etch and anodize wastes was calculated to be sufficient to raise suspension temperature by 30°C, a range of temperatures of from 65 to 90°C was chosen for analysis. Experimental runs 1-3 were therefore conducted at a neutral pH and neutralization temperatures of 65, 80 and 90°C. Initial difficulties did not allow for an analysis of sludge thickening properties at these temperatures for runs 1 and 3. Analyses of interfacial settling velocities were, however, conducted immediately following collection of 18-litres of neutralized sludge for all runs at sludge temperatures of 48, 80 and 72°C for runs 1,2, and 3, respectively. These data are presented in Figures 7.2, 7.3, and 7.4. In addition to settling analyses conducted immediately following neutralization, all sludges were stored at ambient temperature (22-24°C) for 24 hours and examined with respect to thickening properties using interfacial settling analyses. These data are presented in Figures 7.2-7.4 with data collected at the elevated temperatures.

Examination of data collected immediately following waste neutralization, as presented in Figure 7.5, indicated that neutralization temperature did not have a major impact on sludge thickening properties. Although variations were noted in interfacial settling velocities at similar concentrations, these were considered to be within the range of reproducibility of the settling analysis and indicative of virtual identical responses. Data presented in Figures 7.2, 7.3 and 7.4 indicated that analyses conducted after 24 hours of storage and at temperatures which were 33 to 60°C lower than temperatures of neutralization and 22 to 57°C lower than those of initial settling analyses did not change appreciable from those conducted immediately following neutralization. Interfacial settling velocity data for run 2 showed the greatest divergence following storage for 24 hours. Data for this run were also collected with the greatest temperature difference (57°C) and the increased effects of viscosity differences would be expected to have had the greatest impact on these data.

An initial conclusion from these data was that temperature of neutralization did not have a major impact on sludge thickening properties over the range of 65-90°C. In addition, the characteristics of the sludge solids produced at neutralization temperatures of 65-90°C did not change due to aging for a 24-hour period at ambient temperature and appeared to retain physical properties similar to those developed immediately upon precipitation.

Effects of Neutralization pH--

To examine the effects of pH on thickening properties, two experimental runs were made at pH values of 5.5 and 8.5 at a neutralization temperature of 80°C as indicated in Table 7.3. Interfacial settling data were collected immediately following neutralization at 80°C and after a 24-hour storage period at 23°C and are presented in Figures 7.6 and 7.7. The effects of neutralization and ambient temperature on thickening properties were similar to those demonstrated at neutralization temperatures of 65 and 90°C at neutral pH. However, considerable differences resulted from variations in neutralization pH.

Using data presented for run 2 (Figure 7.3) with those for runs 4 and 5, the effect of neutralization pH is indicated in Figure 7.8. Increased pH values resulted in significant increases in interfacial settling velocities at all

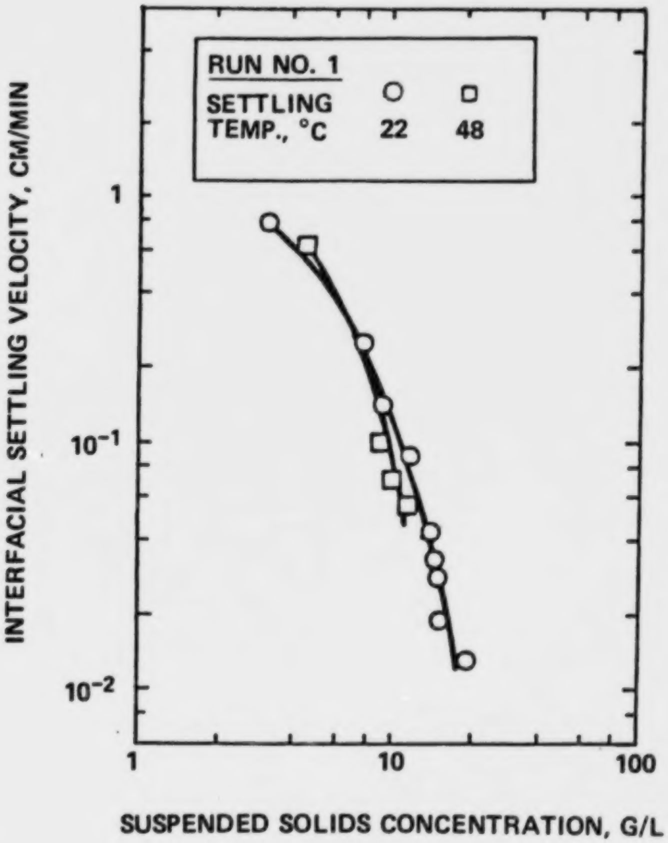

Figure 7.2. Interfacial Settling Velocity Data for Sludge Produced in Run 1.

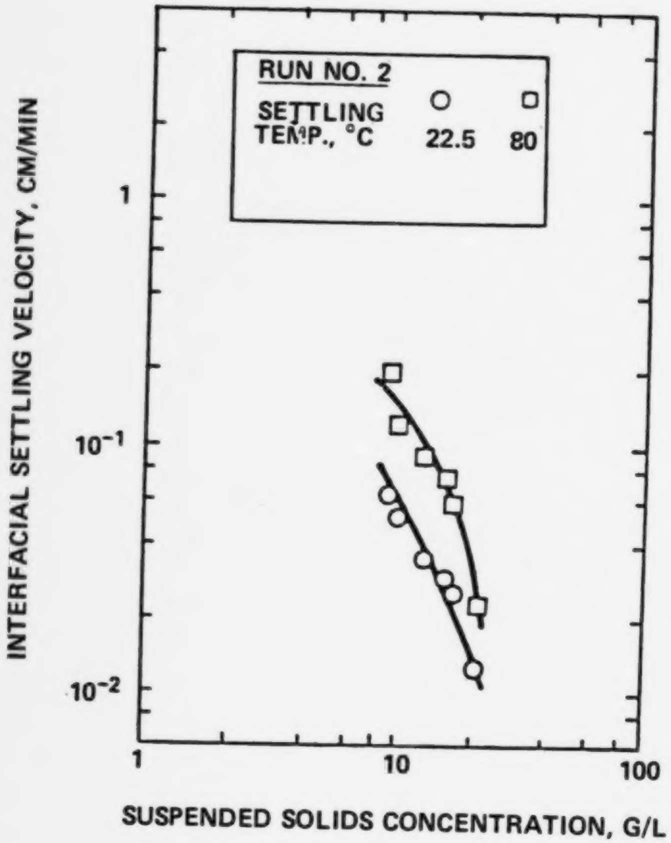

Figure 7.3. Interfacial Settling Velocity Data for Sludge Produced in Run 2.

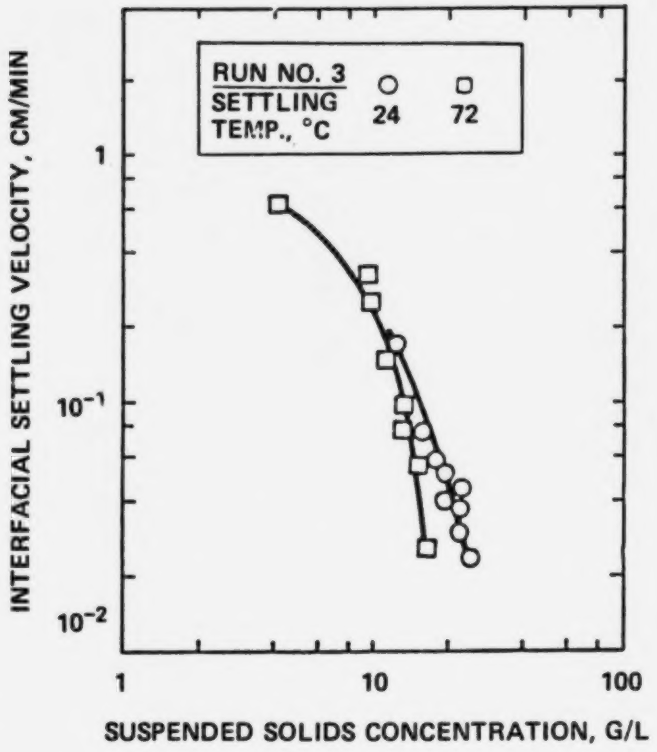

Figure 7.4. Interfacial Settling Velocity Data for Sludge Produced in Run 3.

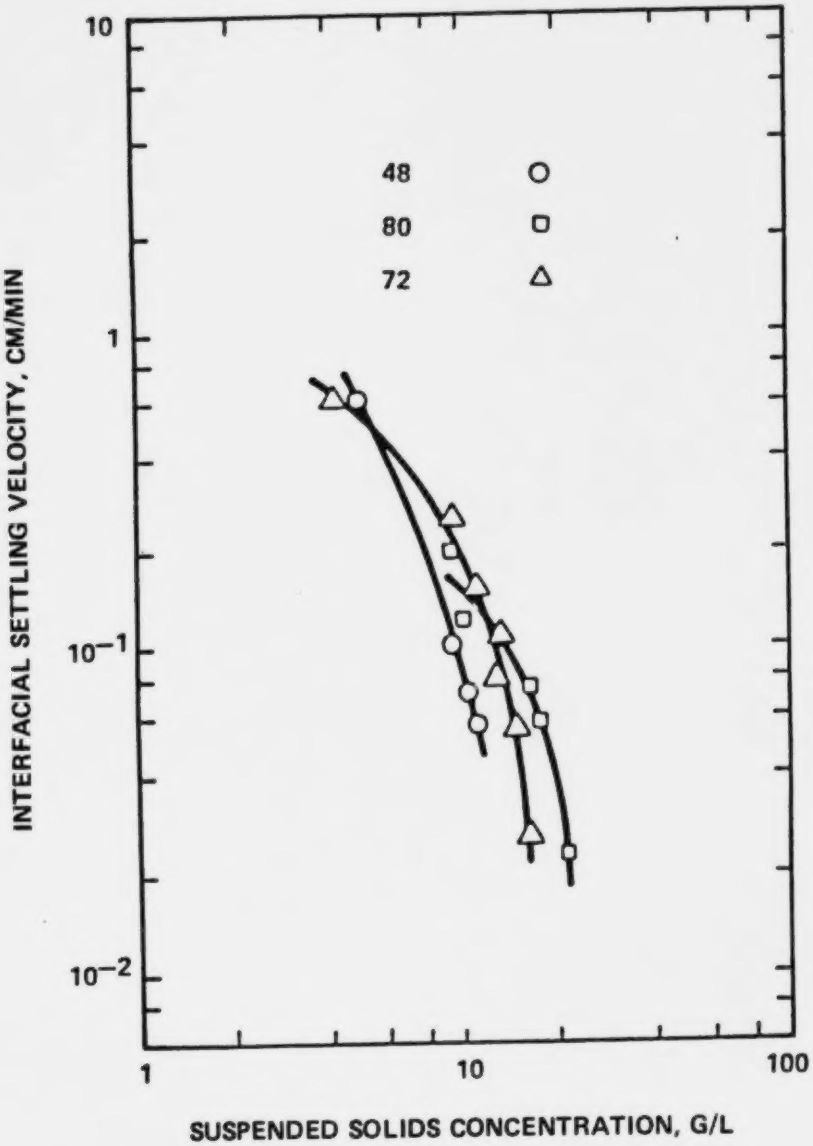

Figure 7.5. Effect of Temperature on Settling Characteristics of Sludges Produced at Elevated Temperatures and Neutral pH.

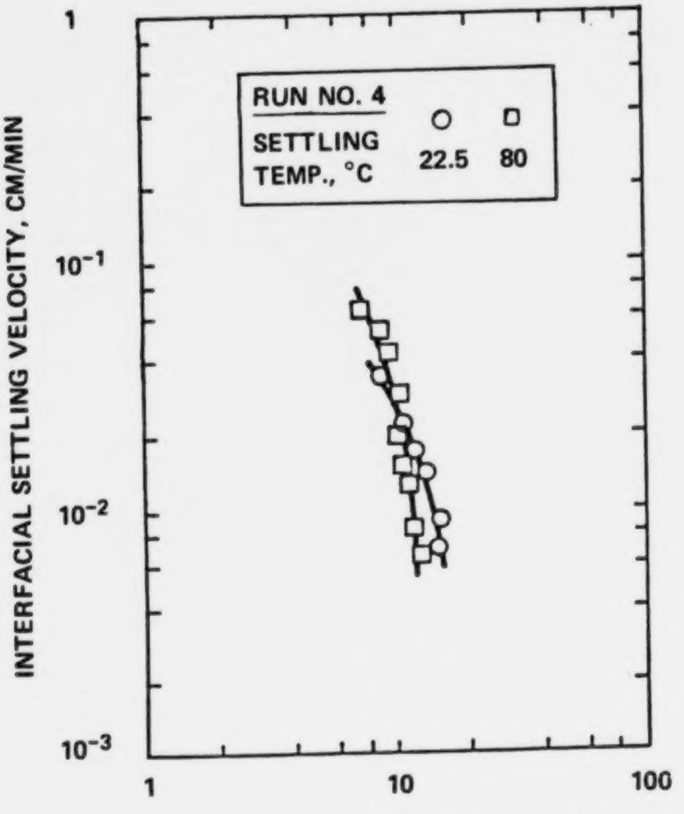

Figure 7.6. Interfacial Settling Velocity Data for Sludge Produced in Run 4.

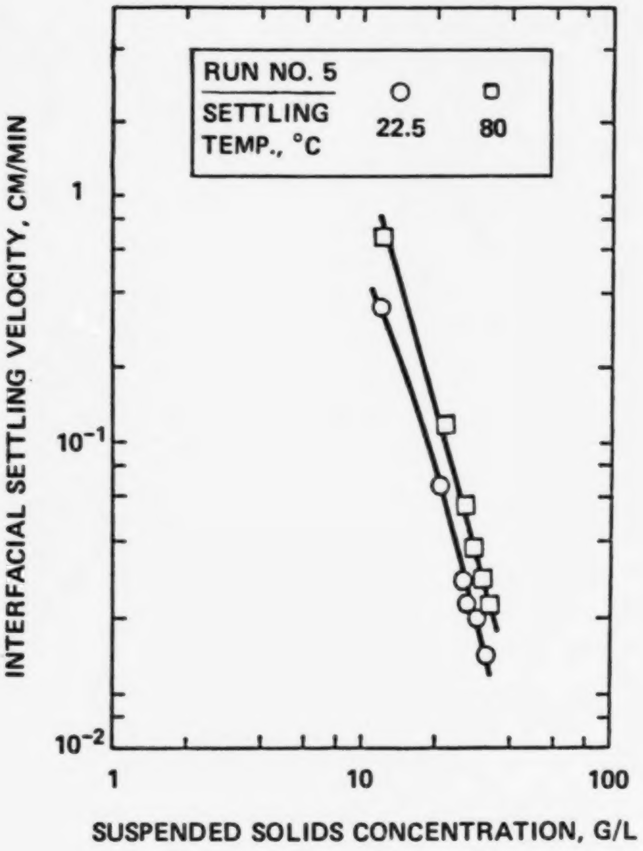

Figure 7.7. Interfacial Settling Velocity Data for Sludge Produced in Run 5.

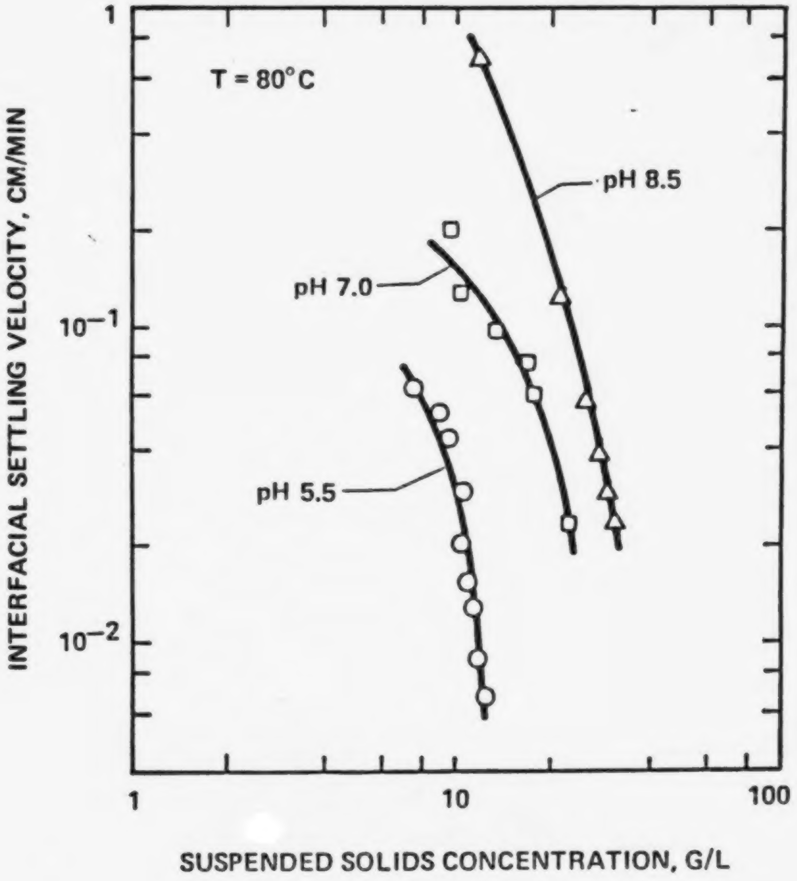

Figure 7.8. Effect of Neutralization pH on Thickening Characteristics of Sludges Produced at 80°C.

suspended solids concentrations. For example, at a suspended solids concentration of approximately 11 g/l, an increase in neutralization pH from 5.5 to 7.0 resulted in more than a 10-fold increase in settling velocity and an increase of pH from 5.5 to 8.5 resulted in a 100-fold increase in settling velocity. Neutralization pH then was a critical variable in segregated neutralization systems and had more impact than did changes in neutralization temperature from 65 to 90°C.

Differences in sludge thickening properties, as indicated by interfacial settling data, are well established with respect to design implications through use of batch flux data, i.e., the product of interfacial settling velocity and suspended solids concentration. Since interfacial settling data for neutral pH values were similar at all temperatures, values at 80°C were used in examining differences in batch flux data. As shown in Figure 7.9, improved thickening properties were apparent for increasing neutralization pH. For example, a sedimentation basin loaded with a solids loading rate of 2 $kg/m^2 \cdot h$ (9.8 $lb/ft^2 \cdot d$) would produce a underflow suspension with a solids concentration of 4.1 percent, 2.8 percent and less than 1.0 percent for suspensions neutralized at 80°C and pH values of 8.5, 7.0 and 5.5, respectively. Therefore, neutralization of concentrated finishing wastes at an alkaline pH would result in the production of a concentrated underflow suspension from a gravity thickener with an effective area less than that required for suspensions neutralized at lower pH values.

PHASE 2 - DEWATERING

Experimental Techniques

A series of dewatering experiments was conducted using one sample of acidic anodize waste and five samples of alkaline etch waste. Multiple etch samples were required since storage for 7 to 10 days resulted in significant changes in etch properties which caused considerable variation in the properties of precipitates formed during neutralization. The acidic anodize waste was stable during storage with respect to analyses conducted. Variations caused by use of numerous samples of spent etch with one anodize waste sample were acceptable since it would, in part, simulate some of the in-plant variations expected with full implementation of segregated neutralization. Characteristics of the concentrated finishing wastes are presented in Table 7.4.

Table 7.4. Characteristics of Waste Solutions Used in Phase 2

Parameter	Sulfuric-Acid Anodize Solution	Spent Etch Solutions				
Experimental Run	1-5	1	2	3	4	5
Temperature, °C	21	50	50	50	50	50
Aluminum, g/l	7.5	51	45.8	28.2	35.6	41.3
Alkalinity, g/l (as $CaCO_3$)	-	405	454	489	454	528
Acidity, g/l (as $CaCO_3$)	340	-	-	-	-	-
pH	0.6	13.5	13.5	13.7	13.3	13.8
Color	Light brown	Dark green	Dark green	Dark green	Dark green	Dark green

*Temperature at time of sampling.

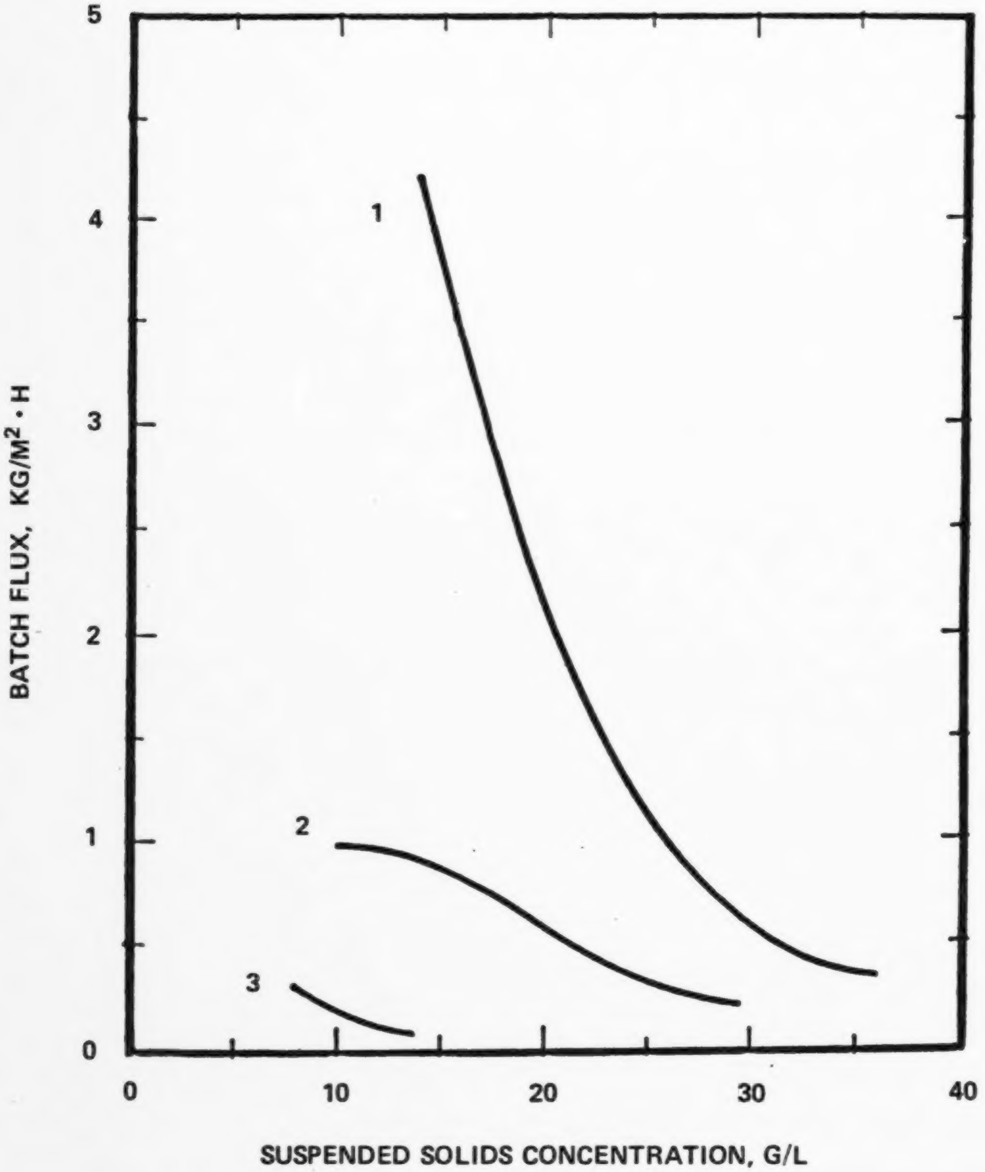

Figure 7.9. Batch Flux Curves at pH Values of 8.5 (#1), 7.0 (#2) and 5.5 (#3).

Spent etch characteristics did not vary drastically and spent etch and acidic anodize solution characteristics were similar to those used in phase 1. Aluminum concentrations were, however, typically lower than those of the initial phase.

Operational parameters used during the five experimental runs are presented in Table 7.5. Since results obtained in the initial phase indicated that neutralization temperature was not a major process variable, 80°C was used as the neutralization temperature for all runs during phase 2. pH was, futhermore, the major process variable and ranged from 5.5 to 10.0. Hydraulic retention time varied between 9.2 and 10.2 min which was similar to phase 1. However, unlike experimental runs made during phase 1, influent concentrated wastes were not diluted but were used full strength.

Table 7.5. Experimental Conditions During Runs in Phase 2

Parameter	Experimental Run				
	1	2	3	4	5
Neutralization pH	8.5	7.0	5.5	10.0	8.5
Neutralization temperature, °C	80	80	80	80	80
Waste Flow Rate					
Anodize Acid, ml/min	28	32	35	28	29
Spent Etch, ml/min	60	66	63	60	60
Hydraulic Retention time, min	10.2	9.2	9.2	10.2	10.2
Suspended Solids*, g/l	101	97	100	86	91

*concentration in neutralized effluent.

Initial examination of specific resistance, filter yield, and CST values for sludges generated in run 1 was focused on determination of the effects of storage for 24 hours at ambient temperature of the suspension produced by neutralization at 80°C. The results indicated that no appreciable differences in sludge dewatering properties resulted from storing neutralized suspensions for 24 hours (Medero, 1981). Since storage allowed for greater flexibility and expansion of experimental investigations for each run, all sludges generated in subsequent runs were examined only at ambient temperature, 25°C.

Experimental evaluations conducted for each sludge suspension produced in runs 1 through 5 were focused on sludge dewatering properties. Specific resistance, filter yield, and capillary suction time (CST) measurements were used throughout to establish sludge dewatering properties as a function of suspended solids concentration. In addition, experimental examinations for runs 1-4 included investigation of the effects of vacuum on specific resistance and filter yield values for one suspended solids concentration. Finally, the effects of time of cake formation on filter yield were examined during runs 2 through 5.

Experimental Results

Run 1--

In this run, sludge solids were produced at a pH of 8.5 and a temperature of 80°C and sludge dewatering analyses were conducted at the neutralization temperature and at room temperature, i.e., 25°C. Data collected at 80°C were similar to those collected at 25°C and are presented elsewhere (Medero, 1981). Specific resistance varied with suspended solids concentration from 1.33×10^{10} to 2.95×10^{10} m/kg, as illustrated in Table 7.6 and Figure 7.10. Cake solids concentration averaged 35.0 percent in specific resistance analyses. The variation of specific resistance with applied vacuum was examined at a suspended solids concentration of 20.8 g/l, from which a compressibility coefficient (S_0) of 1.23 was determined, as illustrated in Figure 7.11.

In filter leaf analyses, filter yield fluctuated with suspended solids concentration from 1.94 $kg/m^2 \cdot h$ at 8 g/l to 104.8 $kg/m^2 \cdot h$ at 157.8 g/l as illustrated in Table 7.6 and Figure 7.10, while cake solids concentration averaged 41.1 percent. The variation of filter yield with applied vacuum was obtained at a suspended solids concentration of 112.1 g/l and is presented in Figure 7.12. A linear correlation was used to describe the variation of filter yield with vacuum at a constant suspended solids concentration. A line with a slope of 1.42×10^{-7} kg/N·s and a least-squares correlation coefficient of 0.975 was obtained for this relationship. However, according to filtration theory, variation of filter yield with vacuum should be a exponential function and data in Figure 7.12 tend to follow such a relationship. This is discussed in detail in a later section.

CST values varied with suspended solids concentration from 23.7 to 59.8 s as shown in Table 7.6 and Figure 7.10.

Run 2--

In this run, sludge was generated at a pH of 7.0 and a temperature of 80°C. Specific resistance varied between 2.33×10^{10} m/kg and 3.18×10^{10} m/kg while cake solids concentration averaged 32.9 percent. These data are presented in Table 7.7 and Figure 7.13. Relationships between specific resistance and applied vacuum were obtained at suspended solids concentrations of 77.9 and 151.1 g/l, for which compressibility coefficients of 0.57 and 0.31, respectively, were obtained as illustrated in Figure 7.14. Filter yield varied from 20.7 $kg/m^2 \cdot h$ at 16.4 g/l to 146.2 $kg/m^2 \cdot h$ at 151.1 g/l as indicated in Table 7.7 and Figure 7.13. Cake solids concentration averaged 34.6 percent solids in these tests. The effects of vacuum and time of cake formation on filter yield were examined at a suspended solids concentration of 151.1 g/l, as illustrated in Figures 7.15 and 7.16. Least-squares correlation coefficients of 0.989 and 0.952 were obtained between filter yield and applied vacuum and between filter yield and time of cake formation, respectively, indicating that linear relationships adequately described these filter yield variations.

Run 3--

In this experimental run, sludge was generated at a pH of 5.5 and a temperature of 80°C and analyzed at room temperature. Variations in specific resistance with suspended solids concentration are presented in Table 7.8 and Figure 7.17. Specific resistance varied from 2.25×10^{11} m/kg to 3.1×10^{11} m/kg and dewatered cakes averaged 31.3 percent solids in these tests. The effect of applied vacuum on specific resistance was examined and compressibility coefficients of 0.42, 0.54 and 0.48 were determined at suspended solids concentrations of 12.8,

Table 7.6. Effect of Suspended Solids Concentation on Specific Resistance, Filter Yield and CST in Run 1 at pH 8.5

Suspended Solids (g/1)	Specific Resistance		Filter Yield		CST
	r (10^{10} m/kg)	Cake Solids (percent)	Y (kg/$m^2 \cdot h$)	Cake Solids (percent)	(second)
20.8	2.09	35.5	1.94	42.9	23.7
64.9	2.95	35.3	15.5	40.7	29.5
112.1	2.00	34.6	27.8	41.3	36.0
135.0	1.33	34.6	53.6	40.4	41.8
157.8	1.56	34.9	104.8	40.0	59.8

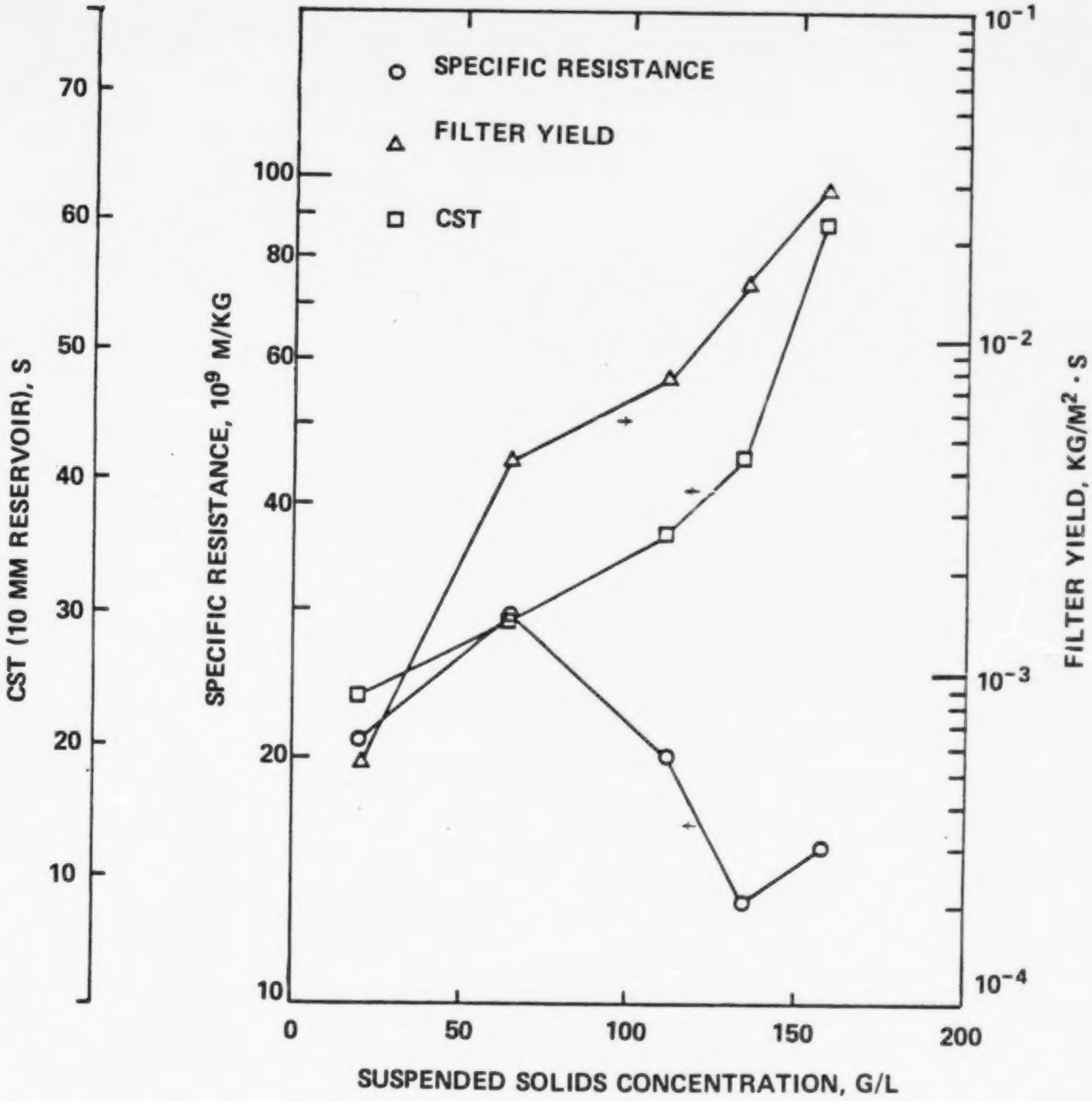

Figure 7.10. Variation of Specific Resistance, Filter Yield and CST with Suspended Solids Concentration in Run 1.

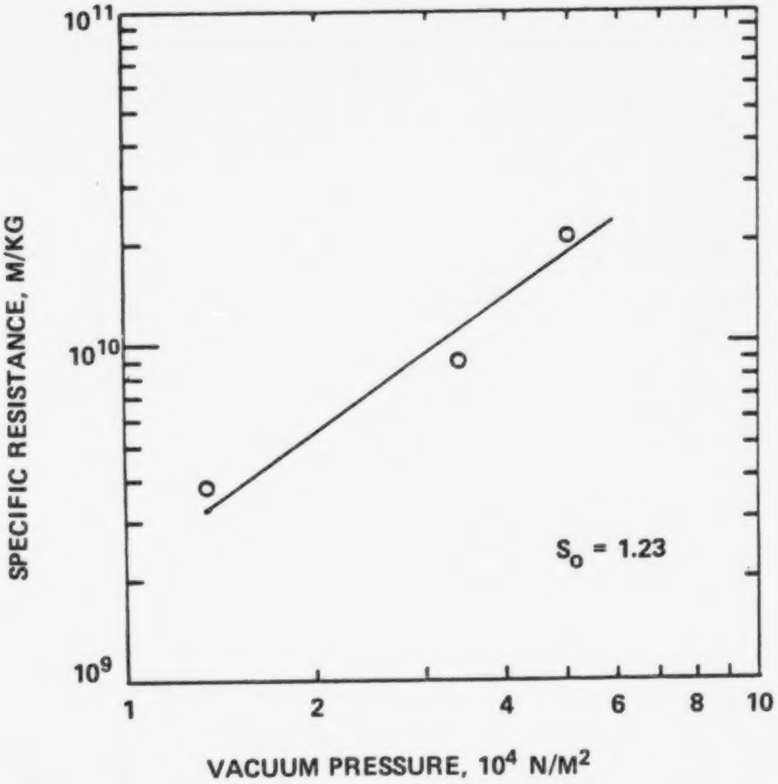

Figure 7.11. Evaluation of Compressibility Coefficient, S_o, at Suspended Solids Concentration of 20.8 g/l for Run 1.

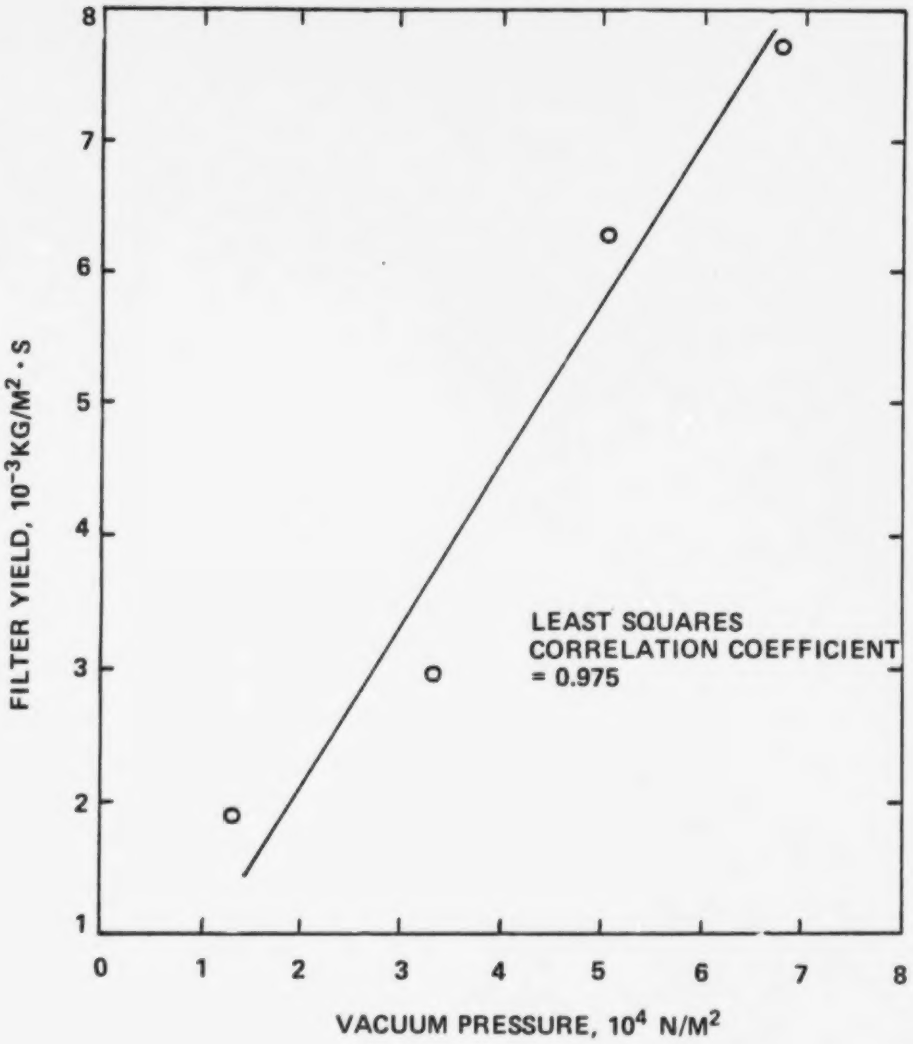

Figure 7.12. Effect of Vacuum on Filter Yield at a Suspended Solids Concentration of 112.1 g/l in Run 1.

Table 7.7. Effect of Suspended Solids Concentration on Specific Resistance, Filter Yield and CST in Run 2 at pH 7.0

Suspended Solids (g/1)	Specific Resistance		Filter Yield		CST (second)
	r (10^{10}m/kg)	Cake Solids (percent)	Y (kg/m^2·h)	Cake Solids (percent)	
16.4	3.18	33.6	20.7	34.8	22.2
48.6	2.64	33.5	48.6	34.3	28.4
77.9	2.76	31.9	72.7	34.6	34.2
112.8	2.33	32.8	101.9	34.5	49.9
151.1	2.37	32.9	146.2	34.6	71.0

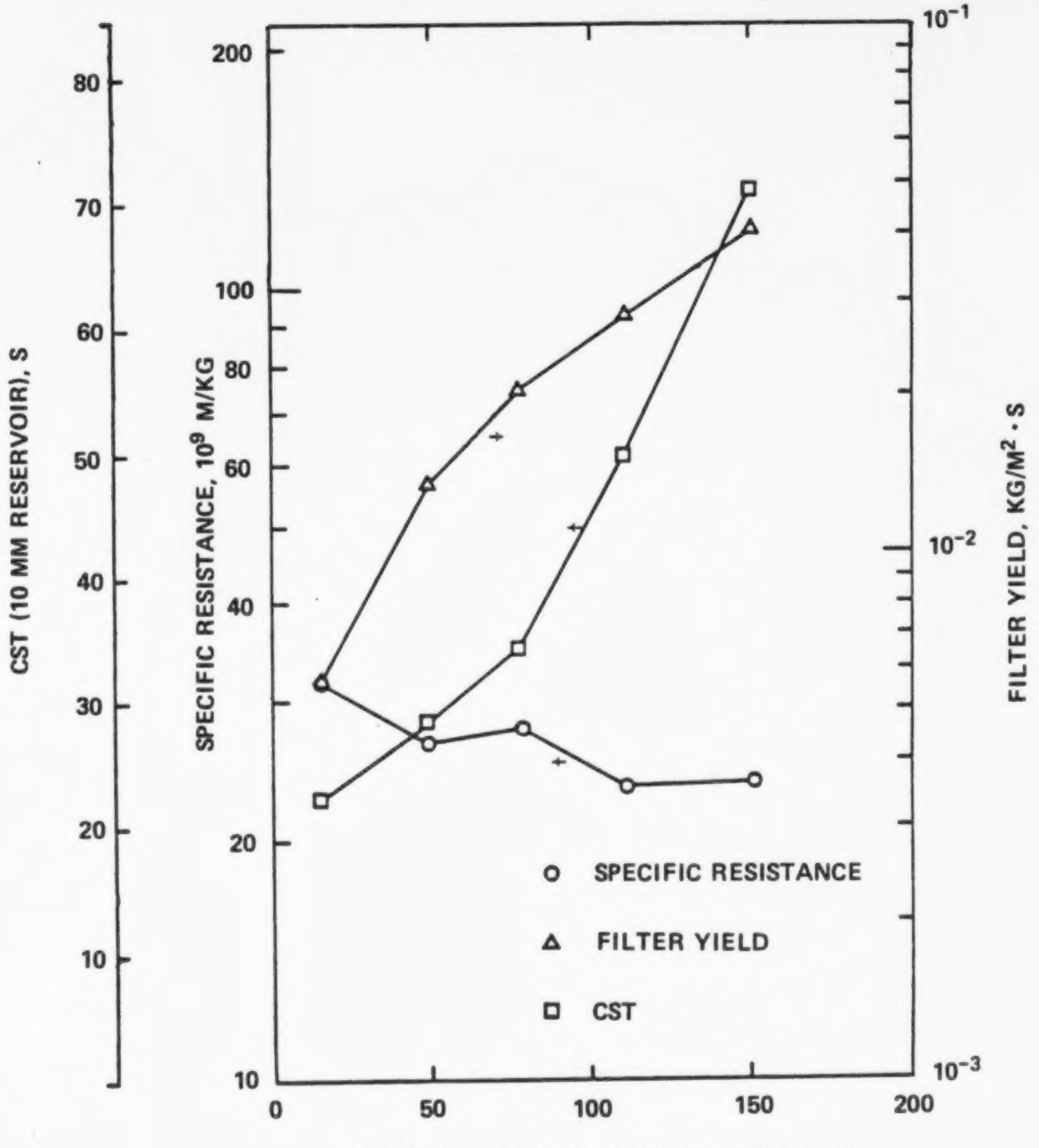

Figure 7.13. Variation of Specific Resistance, Filter Yield and CST with Suspended Solids Concentration in Run 2

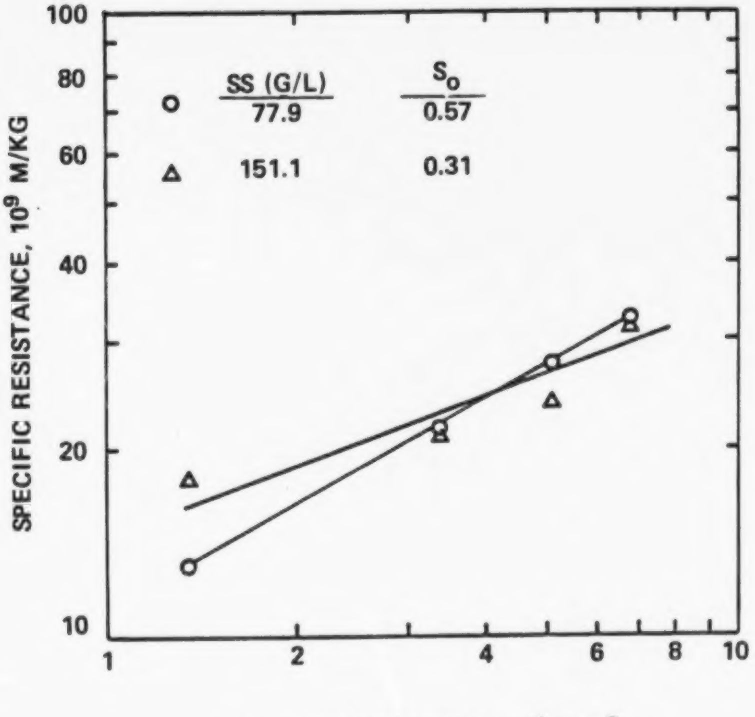

Figure 7.14. Evaluation of Compressibility Coefficient, S_o, at Various Suspended Solids Concentrations for Run 2.

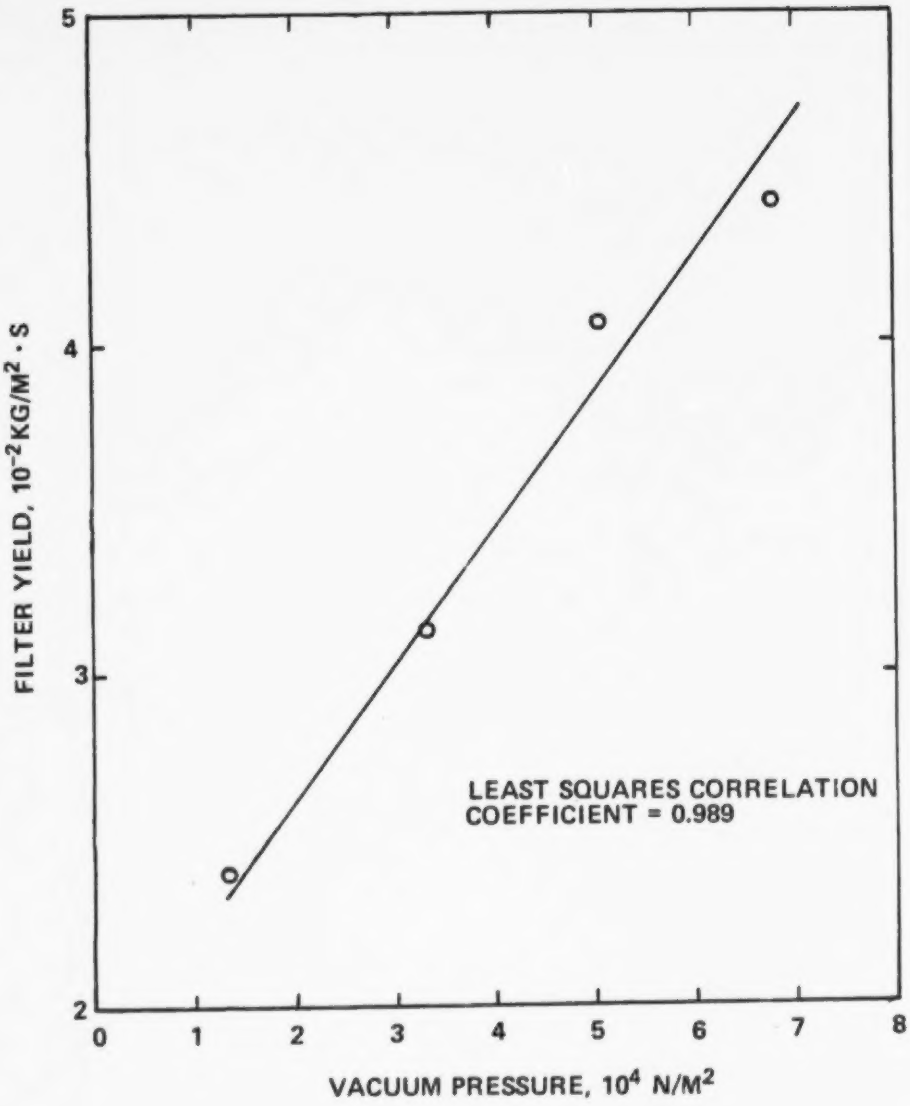

Figure 7.15. Effect of Applied Vacuum Pressure on Filter Yield at a Suspended Solids Concentration of 151.1 g/l and at Room Temperature in Experimental Run 2.

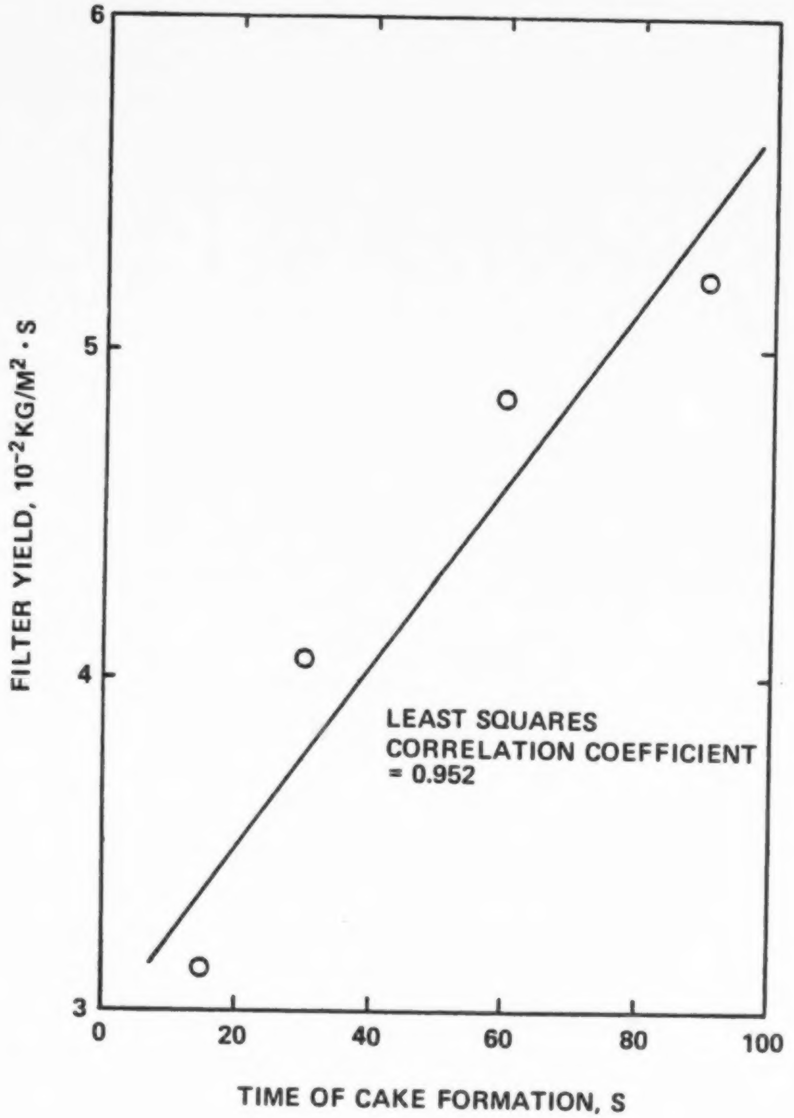

Figure 7.16. Effect of Time of Cake Formation on Filter Yield at a Suspended Solids Concentration of 151.1 g/l and at Room Temperature in Experimental Run 2.

Table 7.8. Effect of Suspended Solids Concentration on Specific Resistance, Filter Yield and CST in Run 3 at pH 5.5

Suspended Solids (g/l)	Specific Resistance		Filter Yield		CST (second)
	r (10^{10}m/kg)	Cake Solids (percent)	Y (kg/m^2·h)	Cake Solids (percent)	
12.8	3.10	32.1	3.55	33.3	38.2
37.1	2.61	32.1	11.6	34.0	64.3
86.5	2.25	30.9	17.4	33.5	123.6
122.8	2.38	30.5	29.1	34.3	170.3
157.5	2.32	46.1	46.1	34.0	255.9

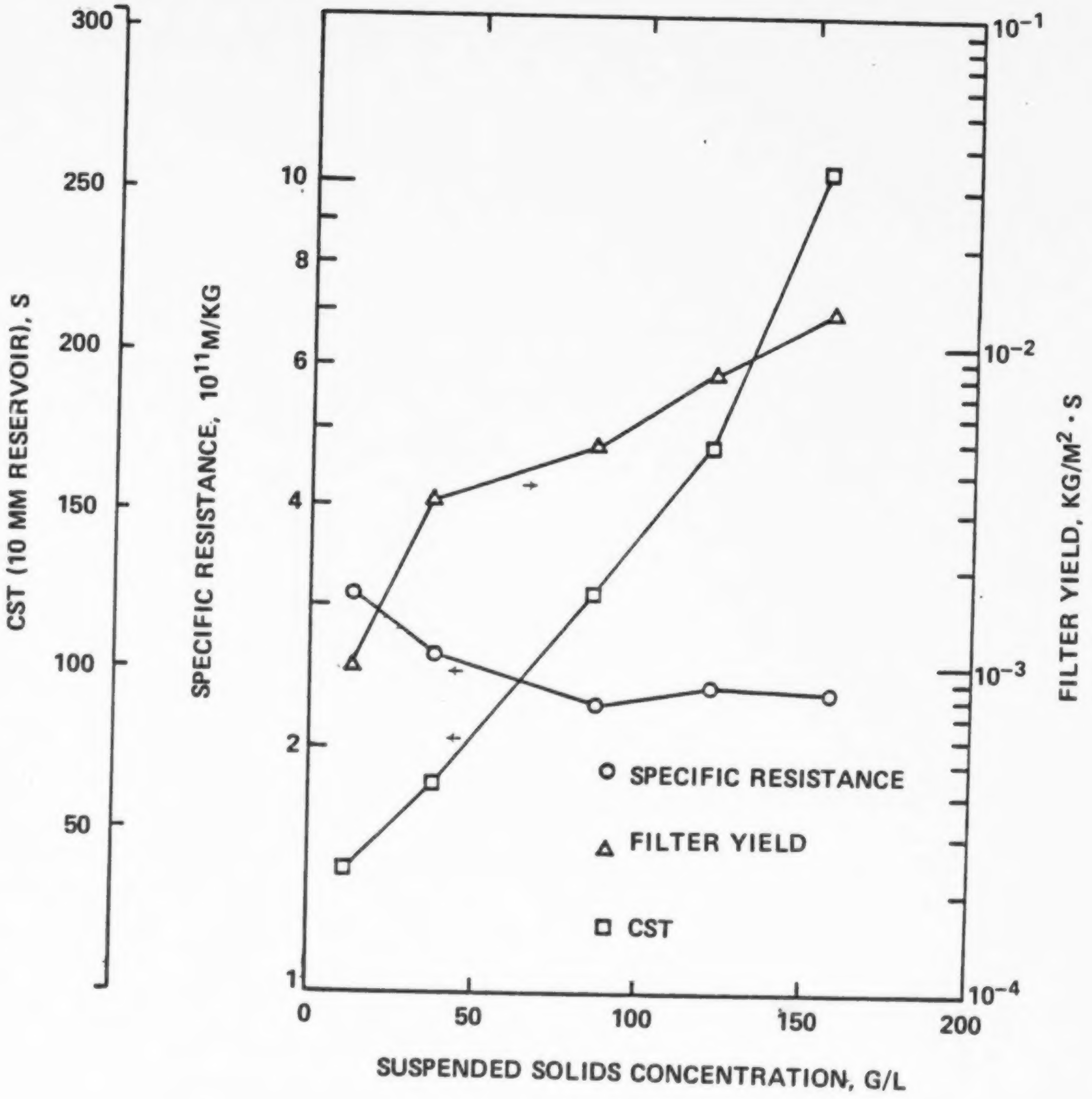

Figure 7.17. Variation of Specific Resistance, Filter Yield and CST with Suspended Solids Concentration in Run 3.

86.5 and 157.5 g/l, respectively, as presented in Figure 7.18. Filter yield varied with suspended solids from 3.55 to 46.1 kg/m^2·h and dewatered cakes from filter leaf tests had an average solids content of 33.8 percent. Variations of filter yield with vacuum and time of cake formation were both obtained at a suspended solids concentration of 157.5 g/l and are presented in Figures 7.19 and 7.20. As shown in the figures, least-squares correlation coefficients of 0.958 and 0.933 were obtained for the relationship of filter yield with applied vacuum and for filter yield and time of cake formation, respectively. CST was observed to vary with feed suspended solids concentration from 38.2 to 255.9 s, as presented in Table 7.8.

Poor dewatering characteristics were observed for this sludge with a neutralization pH of 5.5 when compared to those obtained for sludges in runs 1 and 2. Since dewatering properties deteriorated at this lower pH, a pH of 10.0 was selected for sludge neutralization to evaluate the effect of an elevated pH on dewatering characteristics.

Run 4--

In this experimental run, sludge was generated at a pH of 10.0 and a temperature of 80°C and dewatering analyses were conducted at room temperature. Specific resistance varied with suspended solids concentration from 3.36 x 10^9 to 8.73 x 10^9 m/kg, as illustrated in Table 7.9 and Figure 7.21. The effect of applied vacuum on specific resistance was examined and compressibility coefficients of 0.41, 0.07 and 0.55 were determined at suspended solids concentrations of 25.4, 74.3 and 184.4 g/l, respectively, as presented in Figure 7.22.

Results from filter leaf tests showed a variation of filter yield with suspended solids concentration of from 2.26 to 91.4 kg/m^2·h, as illustrated in Table 7.9 and Figure 7.21. An average value of 48.7 percent solids was obtained for dewatered sludge cakes arising from these tests. The effect of applied vacuum on filter yield was examined at a suspended solids concentration of 184.4 g/l. A linear relationship adequately described the variation of filter yield with applied vacuum at a suspended solids concentration of 184.4 g/l, as illustrated in Figure 7.23. A least-squares correlation coefficient of 0.957 was obtained from this relationship. The effect of time of cake formation on filter yield was examined at a suspended solids concentration of 184.4 g/l. However, as opposed to other sludges generated at 80°C, no definite relationship was observed between these two parameters. However, as illustrated in Figure 7.24, three of the four points presented tended to follow a curve similar to the ones observed in runs 2 and 3 for the relationship of filter yield with cake formation time. The variation of CST with suspended solids concentration was from 23.1 to 51.0 seconds as indicated in Table 7.9.

As observed from data for this and previous runs, the sludge produced at a pH of 10.0 and 80°C showed the best filtration properties in terms of specific resistance and CST. However, it is interesting to observe that the sludge from run 4 exhibited the lowest filter yield values of all the sludges generated in the first four experimental runs. This fact suggested that probably the dewatering characteristics of the suspension generated at the high pH of 10.0 and 80°C were somewhat affected by the sludge particle sizes, as well as other sludge properties.

Run 5--

In this experimental run, sludge was generated at a pH of 8.5 and a temperature of 80°C as in run 1, with the main purpose being to obtain information about

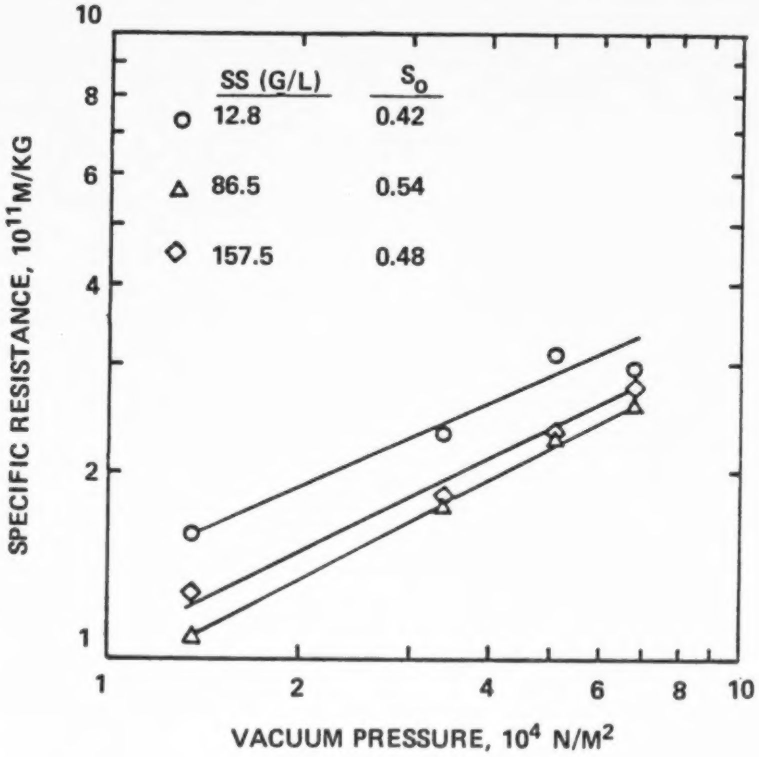

Figure 7.18. Evaluation of Compressibility Coefficient, S_o, at Various Suspended Solids Concentrations in Run 3.

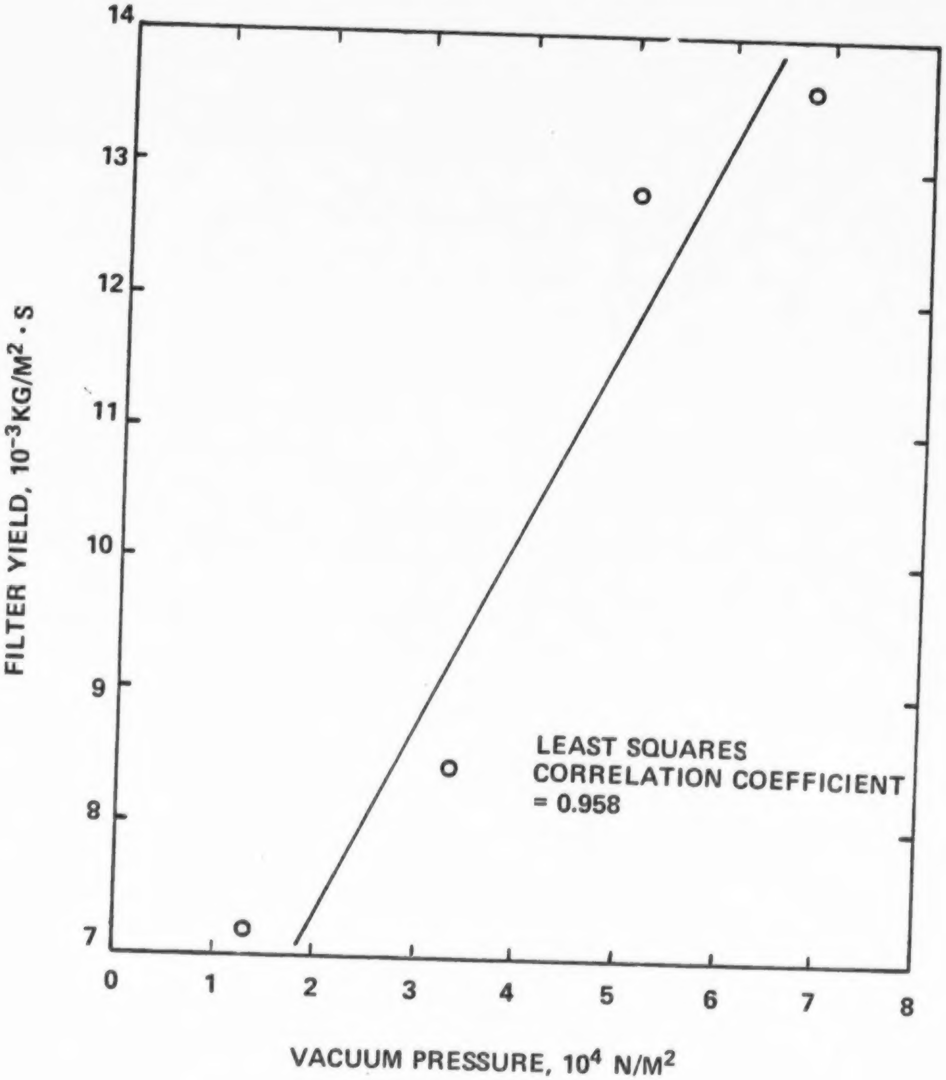

Figure 7.19. Effect of Applied Vacuum on Filter Yield at a Suspended Solids Concentration of 157.5 g/l in Run 3.

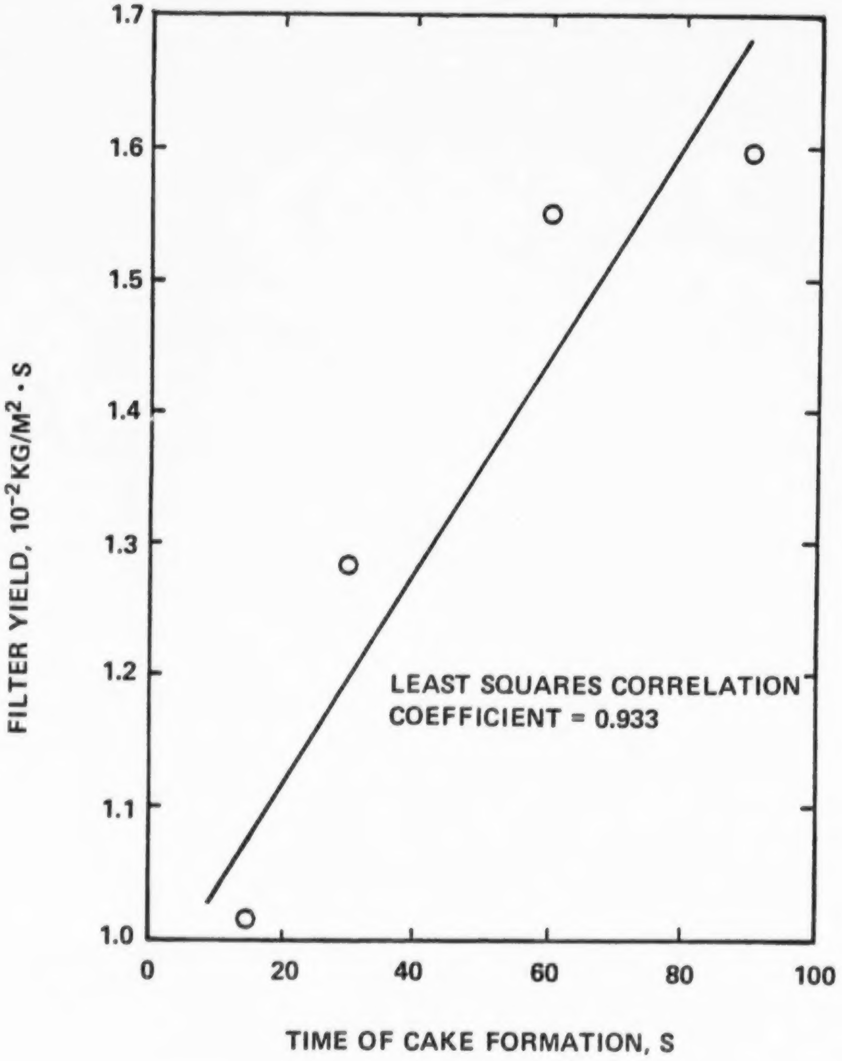

Figure 7.20. Effect of Time of Cake Formation on Filter Yield at a Suspended Solids Concentration of 157.5 g/l in Run 3.

Table 7.9. Effect of Suspended Solids Concentration on Specific Resistance, Filter Yield and CST in Run 4 at pH 10

Suspended Solids (g/1)	Specific Resistance		Filter Yield		CST (second)
	r (10^9m/kg)	Cake Solids (percent)	Y (kg/$m^2 \cdot$h)	Cake Solids (percent)	
25.4	8.73	40.0	2.26	53.8	23.1
74.3	3.85	39.4	-	-	30.7
124.2	3.36	39.0	15,2	44.8	33.6
184.4	4.12	38,8	34.6	48.9	41,5
256.3	5.60	39.5	91.4	47.3	51.0

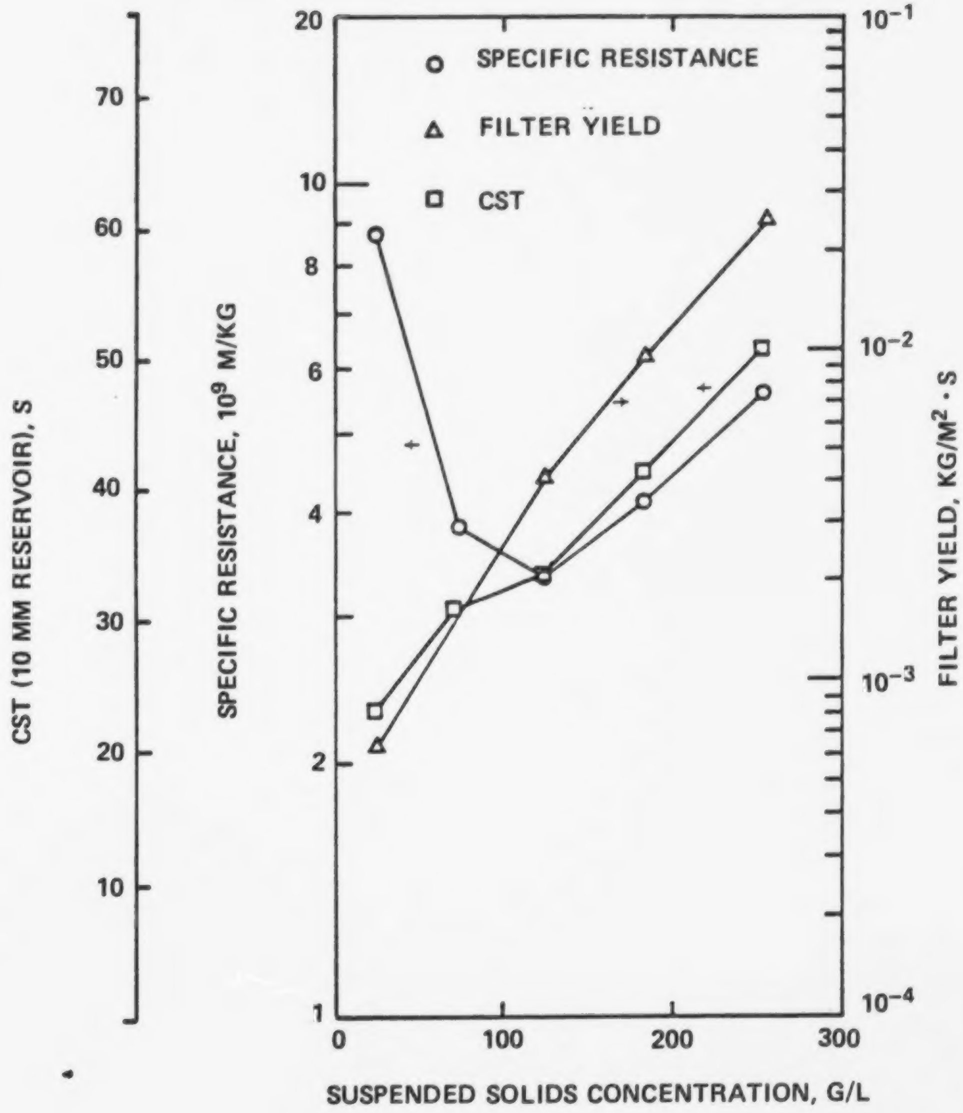

Figure 7.21. Variation of Specific Resistance, Filter Yield and CST with Suspended Solids Concentration in Run 4.

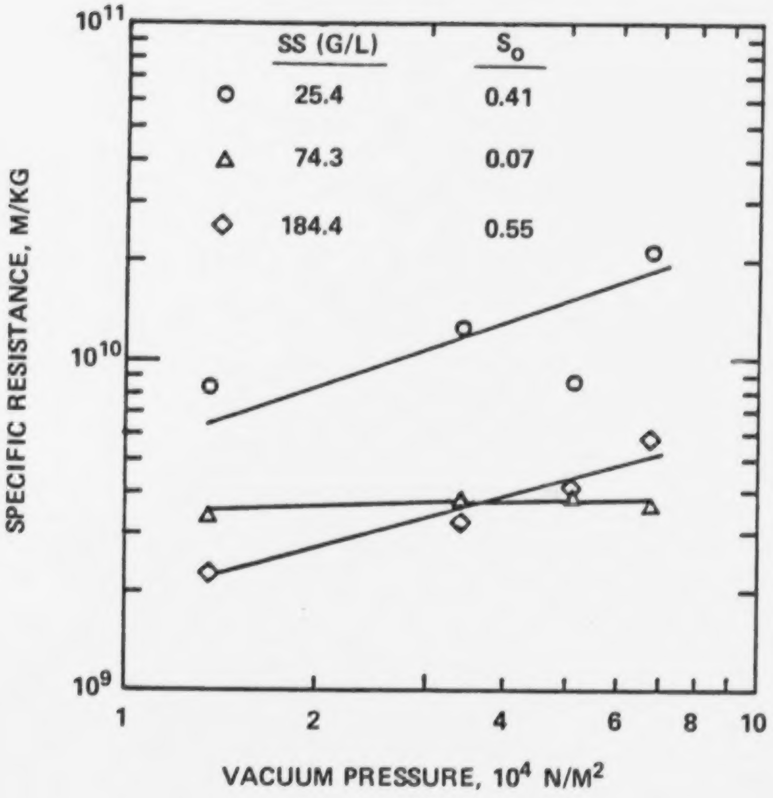

Figure 7.22. Evaluation of Compressibility Coefficient, S_o, at Various Suspended Solids Concentrations in Experimental Run #4.

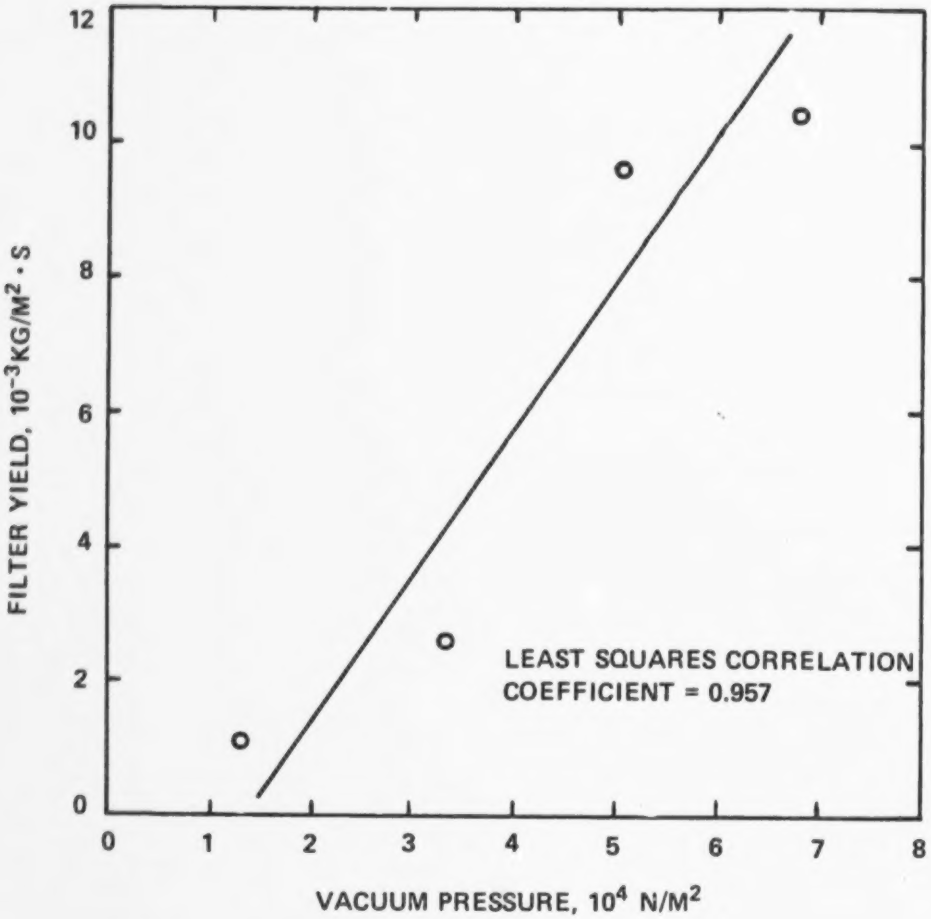

Figure 7.23. Effect of Vacuum Pressure on Filter Yield at a Suspended Solids Concentration of 184.4 g/l in Run 4.

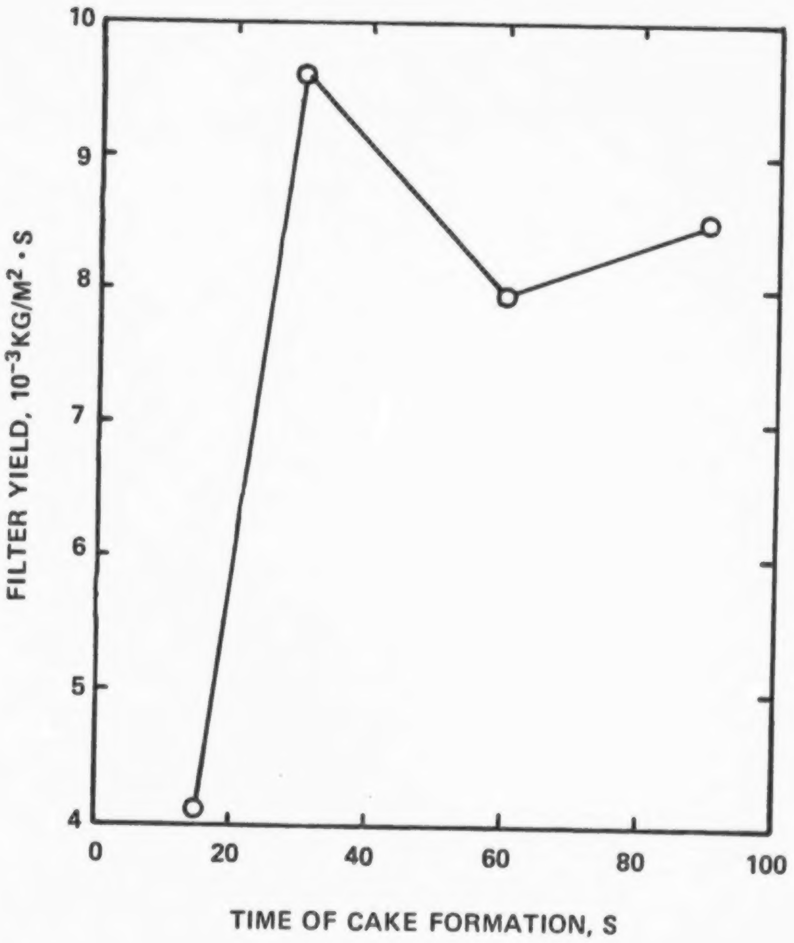

Figure 7.24. Effect of Time of Cake Formation on Filter Yield at a Suspended Solids Concentration of 184.4 g/l in Run 4.

the variation of filter yield with suspended solids concentration at a vacuum pressure of 5.1 x 10^4 N/m^2 (15 in. of Hg). The variation of filter yield with suspended solids concentration for the sludge generated in run 1 was obtained at a vacuum of 6.8 x 10^4 N/m^2 (20 in. of Hg), as opposed to runs 2, 3 and 4 in which a vacuum of 5.1 x 10^4 N/m^2 (15 in. of Hg) was utilized. Therefore, information from run 5 allowed for comparison between filter yield values obtained for the sludge generated at a pH of 8.5 and a temperature of 80°C with the values obtained for other sludges generated at other pH values. In addition, information about the variation of specific resistance and CST with suspended solids concentration was obtained to compare them with the ones obtained previously. Specific resistance varied with suspended solids concentration from 2.87 x 10^9 to 8.45 x 10^9 m/kg, as presented in Table 7.10 and in Figure 7.25. Dewatered cakes averaged 37.4 percent solids in these tests.

The variation of filter yield with suspended solids concentration was observed to be from 18.7 to 525.6 kg/m^2·h as illustrated in Table 7.10 and Figure 7.25. An average of 40.7 percent solids was observed for dewatered cakes arising from these tests. The variation of filter yield with cake formation time was obtained at a constant suspended solids concentration of 159.6 g/l. A linear relationship was observed to be adequate to describe the increase of filter yield with increasing cake formation times at constant suspended solids concentration, as illustrated in Figure 7.26. A least-squares correlation coefficient of 0.946 was determined from the relationship obtained between these two parameters. However, the points illustrated in the figure also tended to follow a similar curve to the ones observed in runs 2 and 3 for the relationship between filter yield and cake formation time. The variation of CST with suspended solids concentration was observed to be from 16.4 to 37.2 s, as illustrated in Table 7.10. These were the lowest CST values observed for all the sludges examined in this study.

Run 6--

In this experimental run, an attempt was made to evaluate the effect of particle size on dewatering characteristics of the aluminum finishing sludges generated at high temperature in this study. This experimental run was conducted with sludges generated in runs 1 to 4 using the specific resistance test with some modifications. The usual filter medium utilized for running specific resistance tests (i.e., Whatman #1 filter paper) was replaced by the filter-leaf media utilized in filter leaf analyses. After filtration of samples, the filtrate was collected and analyzed for suspended solids concentration. The specific resistance values obtained in this run are presented in Table 7.11 and were comparable to specific resistance values obtained previously with Whatman #1 filter media.

Table 7.10. Effect of Suspended Solids Concentration on Specific Resistance, Filter Yield and CST in Run 5 at pH 8.5

Suspended Solids (g/1)	Specific Resistance		Filter Yield		CST (second)
	r (10^9m/kg)	Cake Solids (percent)	Y (kg/m^2·h)	Cake Solids (percent)	
21.0	2.87	37.0	18.7	41.7	16.4
67.5	-	-	33.3	43.3	18.4
113.1	8.45	35.6	69.1	42.4	24.6
159.6	-	-	142.6	39.3	29.9
288.9	4.05	39.7	525.6	36.7	37.2

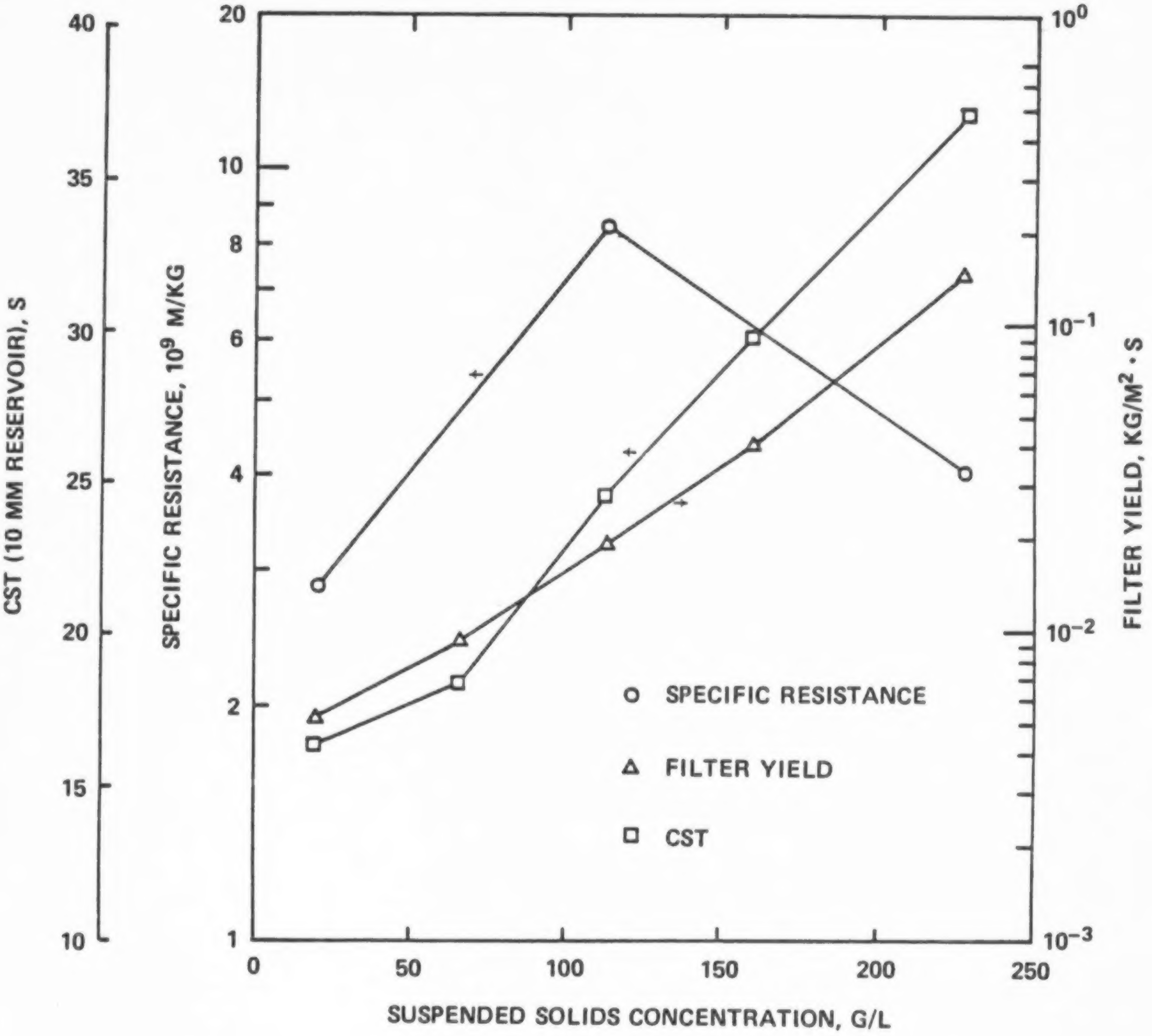

Figure 7.25. Variation of Specific Resistance, Filter Yield and Capillary CST with Suspended Solids Concentration in Run 5.

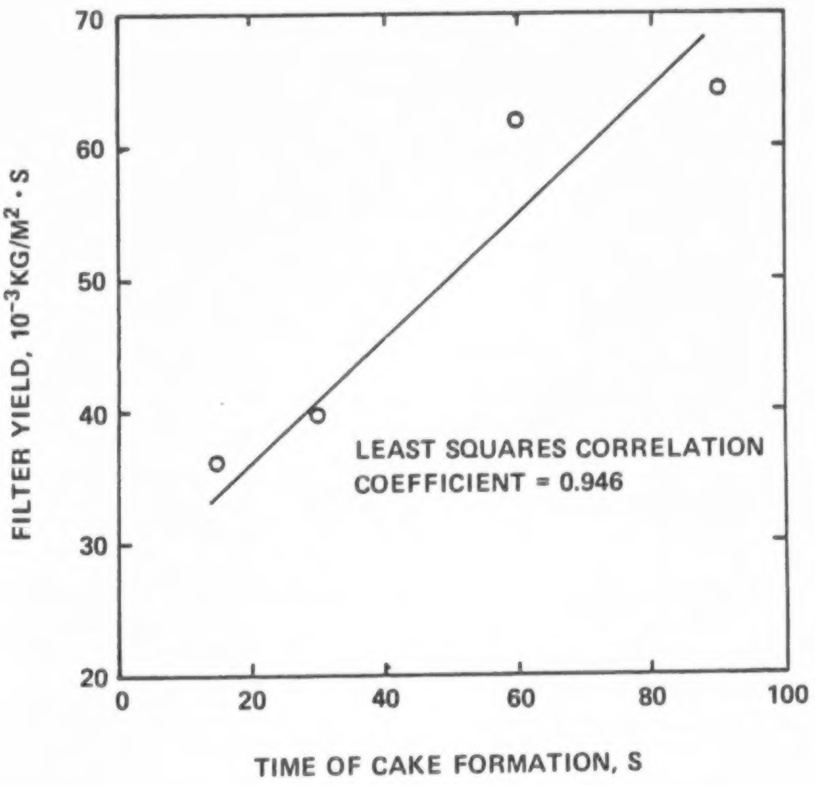

Figure 7.26. Effect of Time of Cake Formation on Filter Yield at a Suspended Solids Concentration of 159.6 g/l in Run 5.

Table 7.11. Results for Specific Resistance Tests in Run 6

Sample From Run	Suspended Solids Concentration Feed (g/l)	Suspended Solids Concentration Filtrate (mg/l)	Specific Resistance r (10^{10}m/kg)	Specific Resistance Cake Solids (percent)
1	157.8	28.0	1.43	37.8
2	112.8	43.4	3.38	32.8
3	157.5	15.3	16.2	41.7
4	184.4	32.2	0.42	40.4

DISCUSSION

Thickening

Evaluation of the impact of segregated neutralization on sludge thickening is facilitated by use of batch flux data in Figure 7.9, in conjunction with similar data for a conventional sludge produced at plant A3 through neutralization of all anodizing wastewaters at ambient temperature and a pH of 7.2. Since the sludge produced by neutralization at pH of 8.5 exhibited the best settling properties of the sludges examined, batch-flux data for this sludge and a conventional sludge from plant A3 (Saunders et al., 1982) are presented in Figure 7.27. The higher flux values for the segregated neutralization sludge indicated improved thickening performance as compared to a conventional sludge.

To evaluate the impact of implementation of segregated neutralization on thickened sludge quantities, an example is presented for a typical extrusion and anodizing plant. The description of the example plant is presented in Table 7.12 and is based on data included in Section 6 and as presented by Saunders et al. (1982). To determine the impact of segregated neutralization on sludge volume, an initial analysis was made assuming that all wastewaters were treated by conventional neutralization and that the batch-flux curve for plant A3 in Figure 7.27 was indicative of thickening properties of this sludge. A second analysis was then conducted assuming that only rinsewater was treated during two shifts and that spent finishing solutions were stored for treatment during a third shift. Therefore, neutralized rinsewater was thickened during two shifts and neutralized spent finishing solutions were thickened in the same sedimentation basin during the third shift. As indicated in Table 7.13, implementation of segregated neutralization results in improved thickening of conventional sludge solids, due to decreased flux rates on the sedimentation basin, and an overall reduction in sludge volume. Using conventional neutralization alone resulted in daily production of 120m^3 of sludge at 12.5 g/l while implementation of segregated neutralization for concentrated finishing wastewaters resulted in daily production of 33.9m^3 of sludge at 44.2 g/l. Although the same mass of sludge solids were produced (i.e., 1.5T/d of dry suspended solids) in each alternative, implementation of segregated neutralization resulted in a 72 percent reduction in sludge volume. Therefore, provision of 56m^3 of storage for concentrated finishing solution

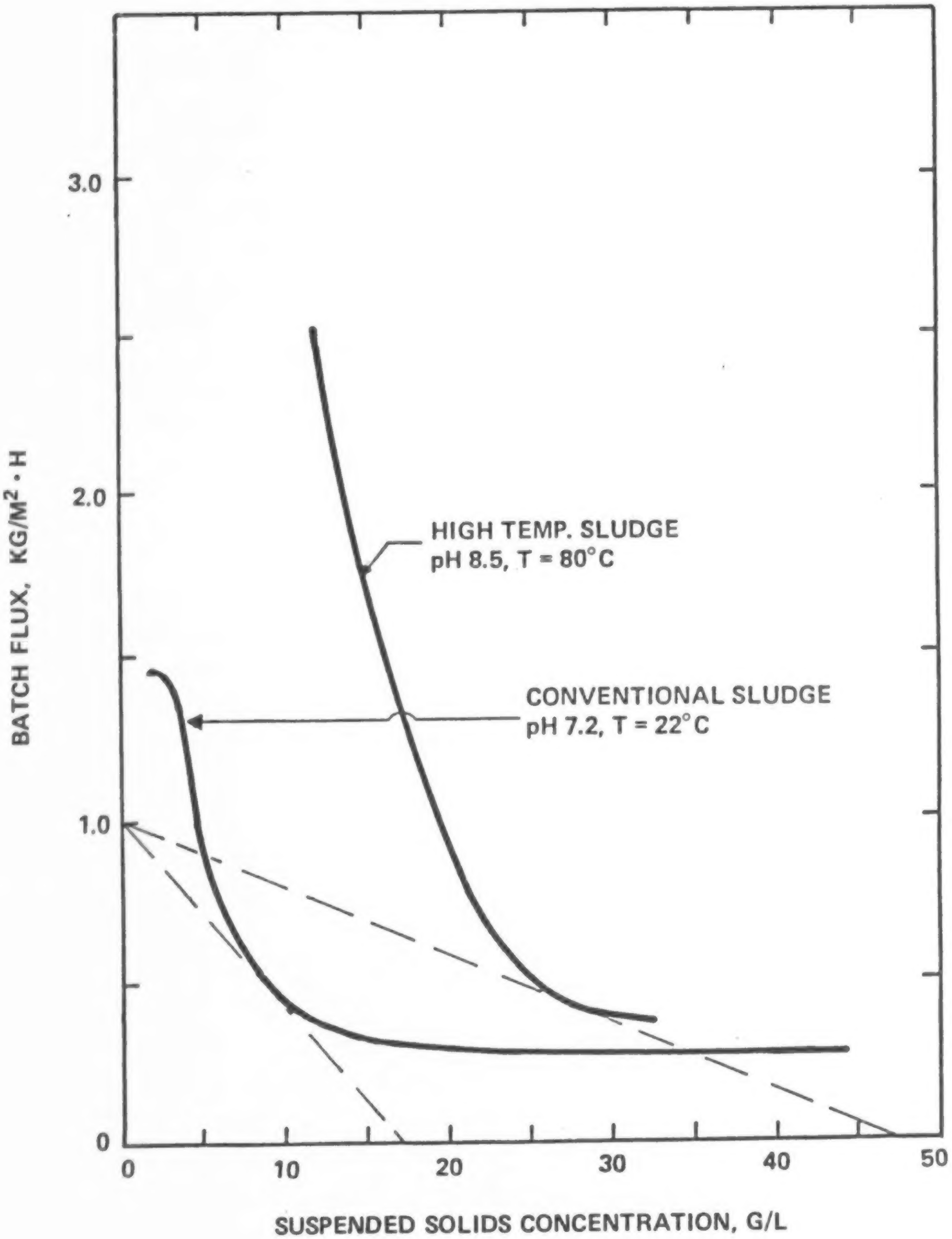

Figure 7.27. Batch Flux Curves for Sludges Produced by Conventional and Segregated Neutralization of Aluminum-Finishing Wastes.

and neutralization of these stored wastes during a third shift would significantly reduce sludge volume.

Table 7.12. Description of Aluminum-Finishing Plant Used in Evaluation of Impact of Segregated Neutralization on Thickened Sludge Volume

Finished Metal Capacity: 20T/d(400T/mo)
Plant Operation: two 8-hour shifts/day
Wastewater Composition
Aluminum Losses: 30g/kg of finished metal
Sludge Aluminum content: 0.4 kg/kg suspended solids
Water Use : $28m^3/T$ of finished metal

Water Sources
Wastewater: 90% = rinsewater
10% = spent finishing solutions
Waste Metal (Al): 30% = rinsewater
70% = spent finishing solutions

Wastewater Treatment
Neutralization Basin
Sedimentation Basin: Surface Area = $65m^2$

Table 7.13. Comparison of the Use of Conventional and Segregated Neutralization at a Typical Aluminum Extrusion/Anodize Plant

	Storage Volume	Thickened Sludge	
	m^3	Concentration g/l	Volume m^3
I. Conventional Neutralization	0	12.5	120
II. Conventional Neutralization with Segregated Neutralization of Concentrated Wastes			
A. Rinsewater	0	54.0	8.3
B. Concentrated Wastes	56	41.0	25.6
C. Total Combined Wastes	56	44.2	33.9

The above example serves to indicate the potential impact of the use of segregated neutralization. In the example, concentrated wastes were neutralized daily. However, this could be performed weekly by providing additional storage volume or could be performed continuously by providing a separate neutralization system. This separate neutralization system would, however, contain only about 10 percent of the volume of a conventional system. Crystalline solids produced during segregated neutralization could be mixed with conventional rinsewaters and settled concurrently. Therefore, the benefits of decreased sludge volumes could be realized at aluminum-finishing plants using numerous treatment strategies. The ultimate benefit in all such cases would be decreased sludge volume which would, for example, decrease sludge transportation costs, decrease volume requirements for sludge lagoons or increase performance of mechanical dewatering systems.

Dewatering

Dewatering properties of sludges produced by segregated neutralization were examined using specific resistance, CST and filter yield measurements, as well as dewatered cake solids, and compressibility coefficient measurements. Process variables which were investigated included neutralization pH and pressure vacuum levels. Initial investigations confirmed that measurements of dewaterability taken immediately following waste neutralization at neutralization temperature (80°C) were virtually identical to those collected after 24 hours of storage at ambient temperature (Medero, 1981). Therefore, all experimental investigations were based on measurements taken after storage for 24 hours at ambient temperature (25°C). The effects of other process variables are examined below.

Neutralization pH--

Specific Resistance and CST-- The relationships obtained between specific resistance and capillary suction time (CST) and suspended solids concentrations for all sludges are illustrated in Figures 7.28 and 7.29. Two relationships are shown in each figure for a pH of 8.5, i.e., runs 1 and 5.

Specific resistance values remained relatively stable with increased suspended solids concentration at all neutralization pH values. This response was typical of such measurements since specific resistance values are normalized to the dry mass of dewatered cake. A decrease in specific resistance, however, was observed with increasing neutralization pH values. Sludge generated at pH 5.5 exhibited the highest specific resistance with values in the range of 2.25×10^{11} to 3.10×10^{11} m/kg. Sludges generated at pH values of 7.0 and 8.5 (run 1) exhibited lower specific resistance values than those observed at pH 5.5. Specific resistance values for these sludges ranged between 1.33×10^{10} and 3.18×10^{10} m/kg. Therefore, sludge neutralized at a pH of 5.5 exhibited specific resistance values which were approximately 10-fold greater than those observed for sludges at pH values of 7.0 and 8.5. A further decrease in specific resistance was observed when neutralization pH was increased to 10.0. Specific resistance values at this pH varied between 3.36×10^9 and 8.73×10^9 m/kg and were from 72 to 75 percent lower than those obtained at pH values of 7.0 and 8.5 in runs 2 and 1, respectively.

The effect of neutralization pH on capillary suction time was similar to that observed for specific resistance, as shown in Figure 7.29. Although no significant differences in CST values were observed at low suspended solids concentrations, definite decreases in CST values were observed with increasing neutralization pH values at high suspended solids concentrations. The highest CST values observed were those for a neutralization pH of 5.5. A significant decrease in CST of

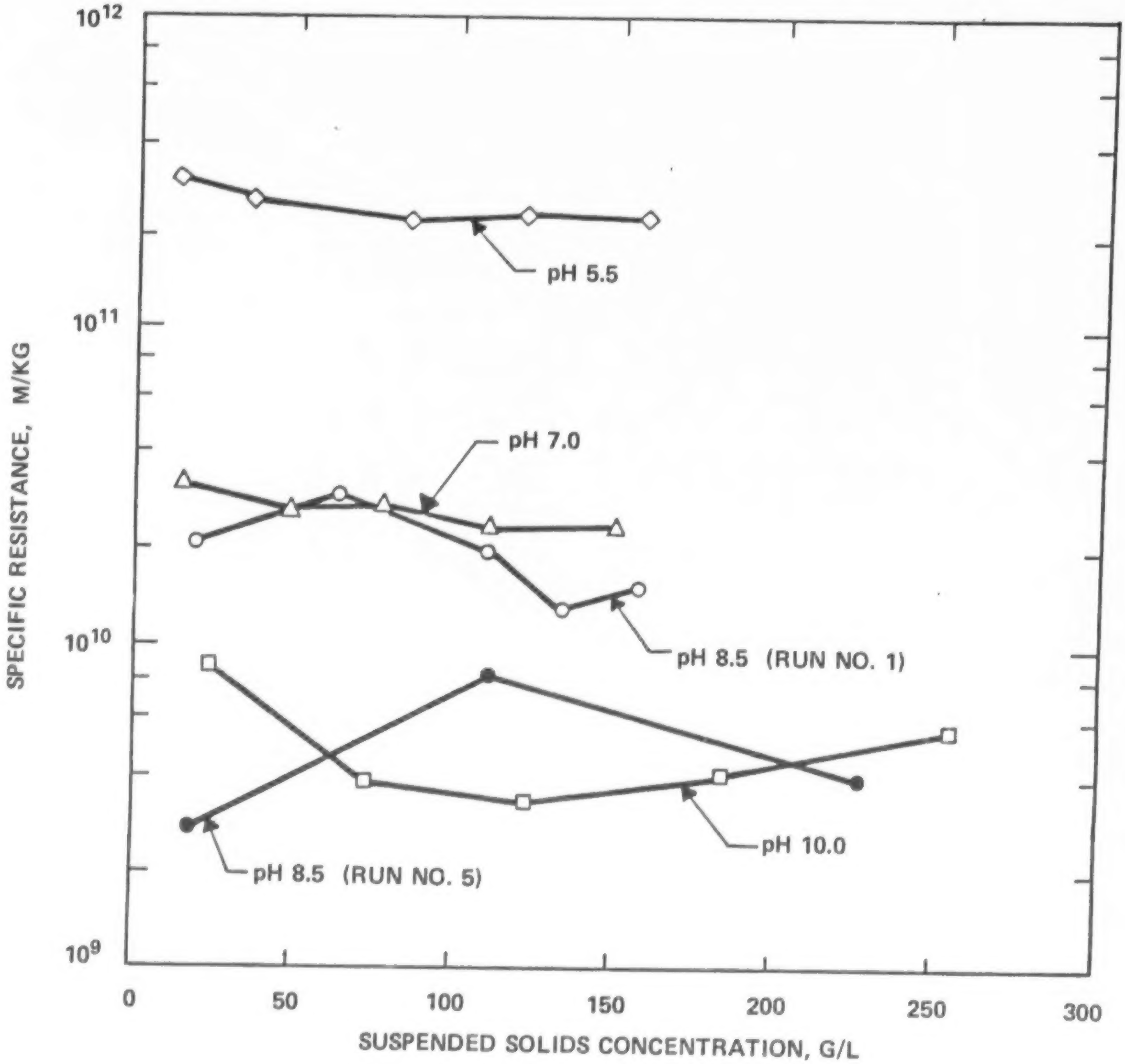

Figure 7.28. Variation of Specific Resistance with Suspended Solids Concentration Produced at Various pH Values.

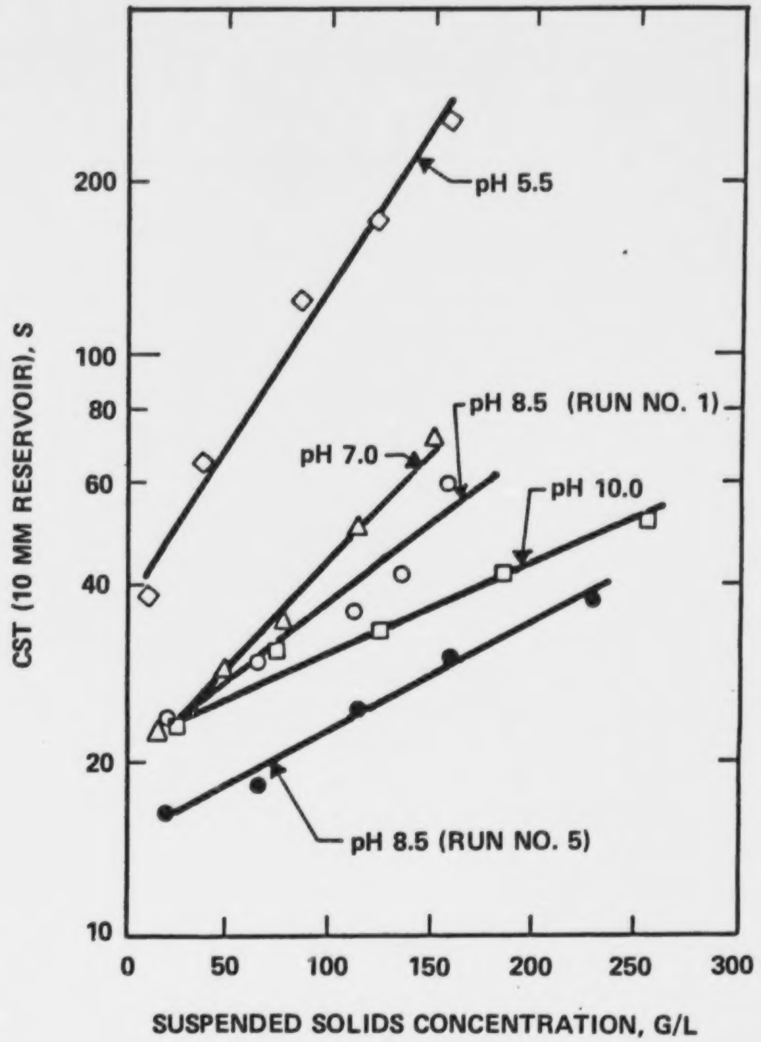

Figure 7.29. Variation of CST with Suspended Solids Concentration at Various pH Values.

between 42 and 72 percent was observed when sludge neutralization pH was increased to 7.0. Sludges produced at pH values of 7.0, 8.5 and 10.0 in runs 2, 1 and 4, respectively, exhibited similar CST values at low suspended solids concentrations whereas, at high suspended solids concentrations, a decrease in CST was observed with increasing neutralization pH. Sludge produced at a pH of 10.0 showed the lowest CST values of the latter three sludges, indicating the best dewatering properties of the sludges examined. CST increased with increasing suspended solids concentration and the rate of increase in CST increased with suspended solids concentration, indicating an exponential relationship. A linear relationship was observed in the semilogaritmic plot in Figure 7.30 of CST and suspended solids concentration and was corroborated by the least-squares correlation coefficients (r) presented in the figure.

As illustrated in Figures 7.28 and 7.29, significant differences were observed for sludges produced at pH 8.5 in runs 1 and 5. The sludge in run 5 had improved dewatering characteristics, in terms of specific resistance and CST, over those in run 1. Also, the sludge in run 5 exhibited the best dewatering characteristics in terms of CST for all the sludges examined. These differences were attributed to changes in waste characteristics since a new etch wastewater sample was used in each one of the runs. However, it is apparent that improved dewatering performance was achieved at pH values of 8.5 (runs 1 and 5) and 10.0 in all cases, when compared to results achieved at lower pH values. Alkaline pH values were therefore indicated to be preferred over neutral and acidic pH values for segregated neutralization.

Filter Yield-- The relationships between filter yield and suspended solids concentration are presented in Figure 7.31. No data are presented for run 1 since filter yield analyses were conducted at a vacuum of 6.8×10^4 N/m^2(20 in. of Hg) as opposed to other sludges in which a vacuum of 5.1×10^4 N/m^2(15 in. of Hg) was used during filter yield analyses.

An increase in filter yield was observed when increasing neutralization pH from 5.5 to neutral and slightly alkaline pH values. However, a subsequent increase in neutralization pH caused a decrease in filter yield. As discussed previously, specific resistance and CST values for these sludges decreased with neutralization pH, indicating that improved filtrability could be achieved by increasing neutralization pH values. This would indicate that higher filter yields could be obtained when increasing neutralization pH under practical conditions. However, since filter leaf tests provide a realistic approximation of vacuum filter operation, filter-leaf data were used in selecting optimum neutralization pH for improving sludge dewatering characteristics at the reference plant.

As observed in Figure 7.31, filter yield values of sludges at various pH values increased with suspended solids concentration and the highest filter yield values were observed for sludges neutralized at pH values of 7.0 and 8.5. For the sludge generated at a pH of 5.5, filter yields were 68 to 91 percent lower than those observed at pH values of 7.0 and 8.5.

The sludge produced by neutralization at a pH of 10.0 exhibited the lowest filter yield values for all the sludges examined. Filter yield values for this sludge ranged from 2.3 to 91.4 kg/m^2·h. This sludge, however, showed excellent filtration properties in terms of specific resistance and CST when compared to other sludges examined, indicating that high filter yields would have been expected. Therefore, filter yield data obtained for this sludge suggested

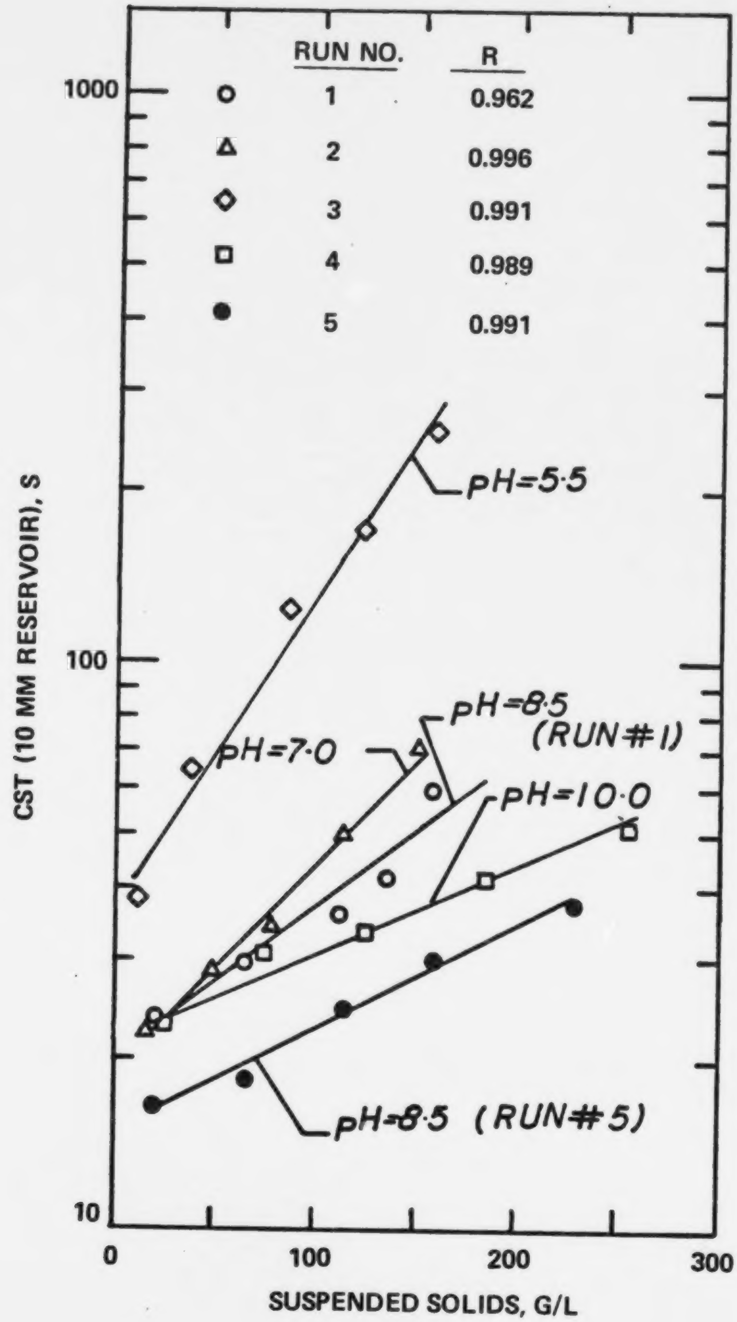

Figure 7.30. Variation of CST with Suspended Solids Concentration at Various pH Values.

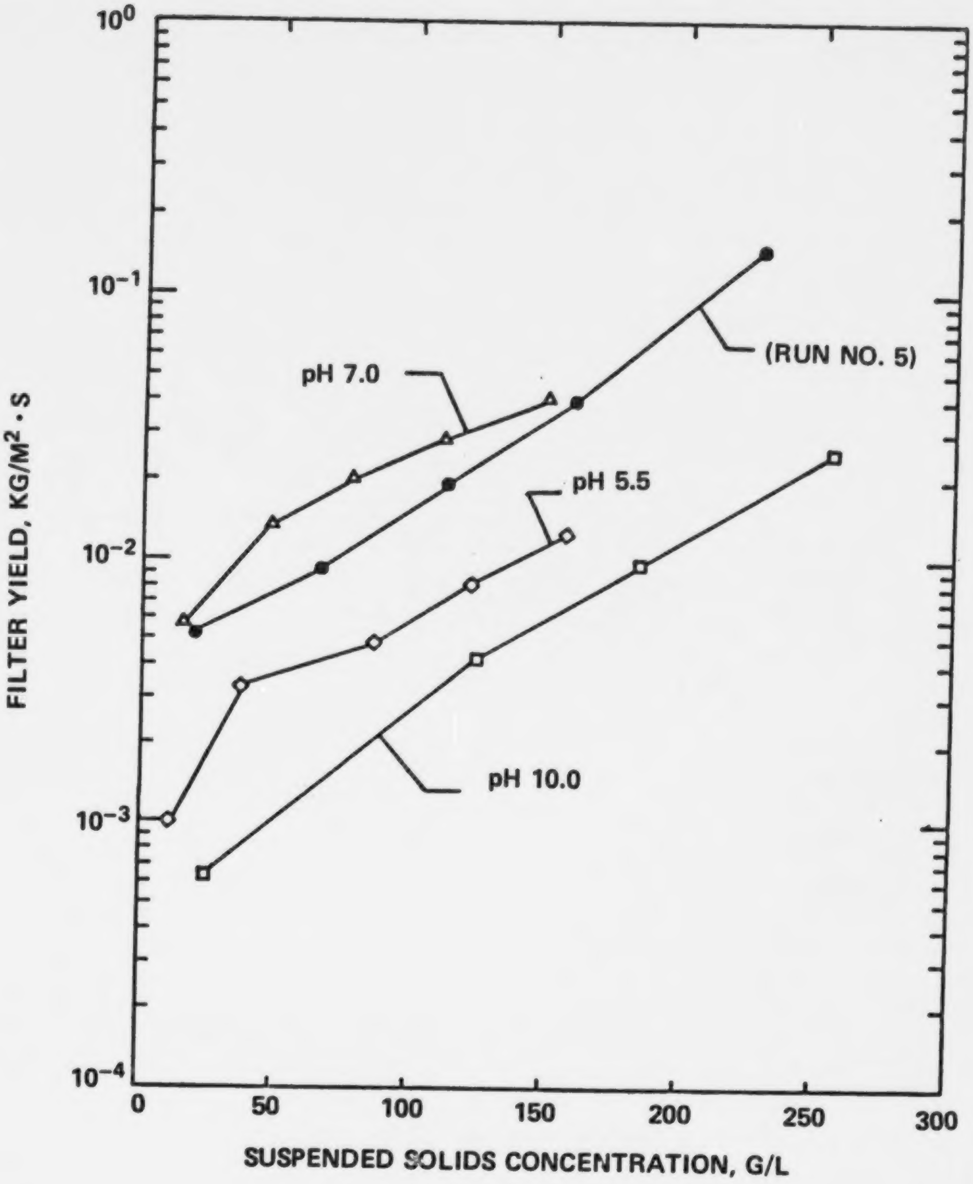

Figure 7.31. Variation of Filter Yield with Suspended Solids Concentration at Various pH Values.

that filtration characteristics might have been affected by small particles causing blinding of the filter-leaf medium during filtration. If this were the case, however, specific resistance of the sludge would increase as a result of blinding during filter-leaf analysis. Comparison of specific resistance results obtained with media typically used with the specific resistance test (i.e., Whatman No. 1 paper) with specific resistance results obtained with the media used on the filter-leaf apparatus (i.e., NY-319F 3/1 Br Twill multifilament cloth) indicated that media blinding was not an apparent cause of the unusually low filter yield data (Medero, 1981). Low filter yields observed for the sludge at a neutralization pH of 10.0 could also be attributed to settling of the sample during filter-leaf analysis. Good settling characteristics were expected for the sludge, which showed excellent filtration properties in terms of specific resistance and CST. Slow agitation provided in the filter-leaf analysis could have been insufficient to keep the solids in suspension resulting in blinding of the filter by small particles and decreased accumulation of solids on the filter surface. Therefore, it is apparent that at a neutralization pH of 10.0, a sludge that exhibits good dewatering properties may be otained but, unfortunately, the sludge would probably cause operational problems during vacuum filtration either by settling or other unknown conditions, resulting in low filter yields. Consequently, larger vacuum-filter surface areas would be required to dewater the sludge.

The optimum neutralization pH for improved sludge dewatering properties by segregated neutralization of spent etch and anodize wastewaters an an aluminum-finishing plant appeared to be in the range of 7.0 to 8.5. Selection between these values of neutralization pH is affected by the solids or moisture content of the cake solids produced by dewatering.

Cake Solids-- The relationship between cake solids concentration and suspended solids concentration obtained from filter-leaf analyses are presented in Figure 7.32. Cake solids concentrations ranged from 33 percent to 53 percent solids and were much higher than cake solids concentrations typically achieved with conventional aluminum-finishing sludges. In addition, cake solids contents increased as neutralization pH increased. The excellent dewatering properties of the sludge produced at a neutralization pH of 10.0 were enhanced by a high cake solids concentration after dewatering, with cake solids content fluctuating between 45 and 53 percent, which were the highest values observed. Sludge produced at a neutralization pH of 7.0 had cake solids concentrations of 34 to 35 percent. These were only slightly higher than those for sludge produced at a neutralization pH of 5.5, which was the sludge with the poorest dewatering properties of all the sludges examined. Sludge produced at a neutralization pH of 8.5 had cake solids concentrations ranging from 37 to 43 percent and were greater than those observed for the sludge produced at a neutral pH.

Examination of Figures 7.28, 7.30 and 7.32 indicated that of all sludges examined, the sludge produced at a neutralization pH of 8.5 exhibited the best overall dewatering characteristics, especially when filter yield values and cake solids content were considered. Sludges produced at a higher pH had increased solids contents but lower filter yields while sludges produced at lower pH values had lower dewatering rates and lower cake solids contents. Therefore, from the studies presented herein, it is apparent that a neutralization pH of 8.5 produced the best sludge properties and should be more closely examined in a pilot-scale system.

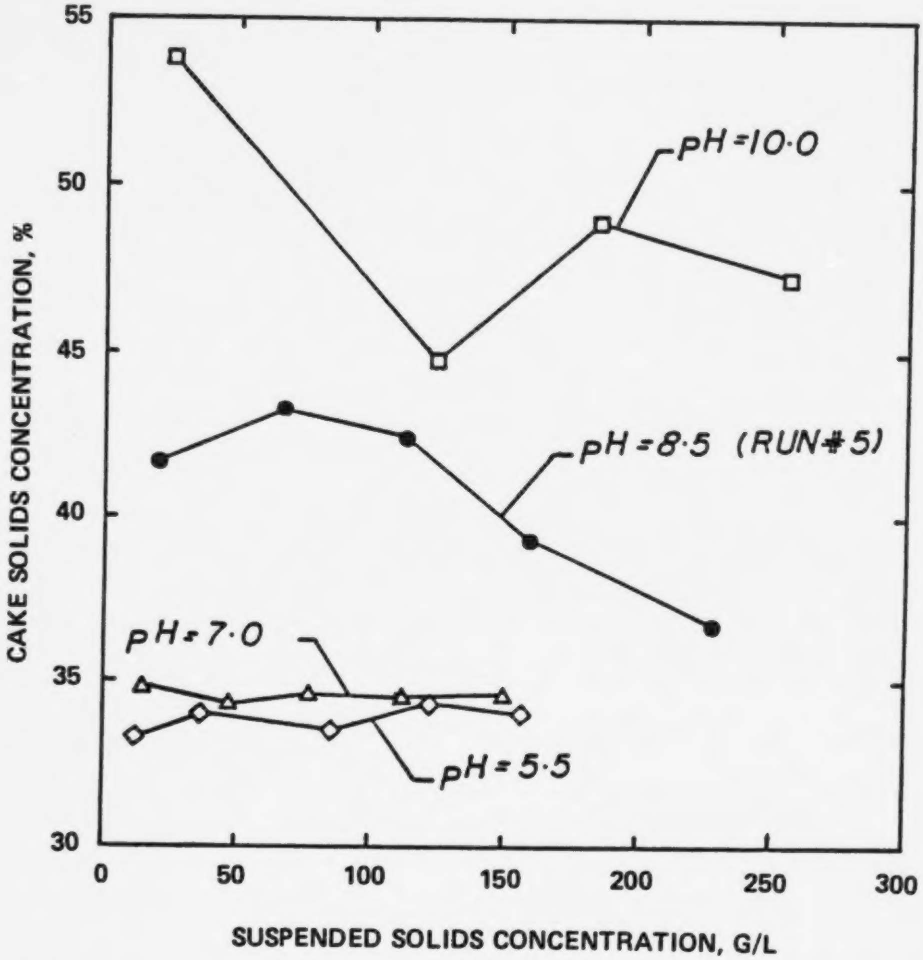

Figure 7.32. Effect of Suspended Solids Concentration on Cake Solids Concentration in Filter-leaf Analyses for Various Neutralization pH Values.

Sludge Compressibility--Compressibility coefficients (S_0) were obtained for segregated neutralization sludges at various suspended solids concentrations using specific resistance measurements to obtain average values for each suspension. Compressibility values ranged from 0.34 to 1.23 and were in the range of compressibility coefficients reported for alum sludges resulting from the treatment of surface waters for drinking purposes (Novak and Montgomery, 1975; Novak and Langford, 1977; Glenn et al., 1973; Ball, 1978).

Compressibility coefficients are measures of variations of sludge specific resistance with vacuum pressure. A sludge of high compressibility produced an impervious cake at high vacuum due to squeezing and compaction of the sludge cake during sludge filtration, therefore, increasing sludge resistance to filtration and decreasing sludge yield on a mechanical filter. Therefore, sludge compressibility should decrease with an improvement in dewatering properties of the sludge.

Average compressibility coefficients obtained for sludges produced at the four neutralization pH values examined are presented in Figures 7.33. With the exception of the value of S_0 = 1.23 at a pH value of 8.5 (run 1), coefficients of compressibility decreased with increasing neutralization pH. The value determined in run 1 was for a single, dilute (20.8 g/l) suspension while all other values were determined using two to three concentrated suspensions. Difficulties associated with determination of specific resistance of dilute suspensions could therefore account for this single extraneous value. Using the dotted line in Figure 7.33, a correlation coefficient of 0.999 was obtained. It was therefore apparent that sludge compressibility decreased with increasing neutralization pH values and that the low values were indicative of sludges with excellent dewatering properties.

Vacuum Pressure--

As indicated in Figure 7.34, filter yield increased with vacuum pressure for all sludges at constant initial suspended solids concentrations. The increase was well described by a linear relationship as indicated by least-squares correlation coefficients of 0.956 to 0.989. Therefore, filter yield increased in direct proportion to the vacuum pressure indicating that greater solids capture could be achieved by increasing vacuum pressure with a subsequent decrease in the vacuum-filter surface area required to dewater these sludges at a constant initial suspended solids concentration.

The variation of cake solids concentrations with vacuum obtained from filter leaf tests for each sludge is presented in Figure 7.35. An increase in cake solids concentration was observed with increased vacuum and the rate of increase of cake solids with vacuum pressure was constant for all sludges examined. Therefore, at a constant initial suspended solids concentration an increase in vacuum pressure increased sludge solids content making the sludges more manageable and amenable to ultimate disposal.

Comparison of data in Figure 7.35 developed with filter-leaf analyses with those in Figure 7.32 from specific resistance analyses indicated that sludges produced at a neutralization pH of 10 had the highest solids content following dewatering in both analyses. In addition, sludge produced at a neutralization pH of 8.5 had the next highest cake solids content followed by those produced at pH values of 5.5 and 7.0. Therefore, increased neutralization pH resulted in production of dewatered cakes with higher solids contents which could be more effectively dewatered with increases in vacuum pressure.

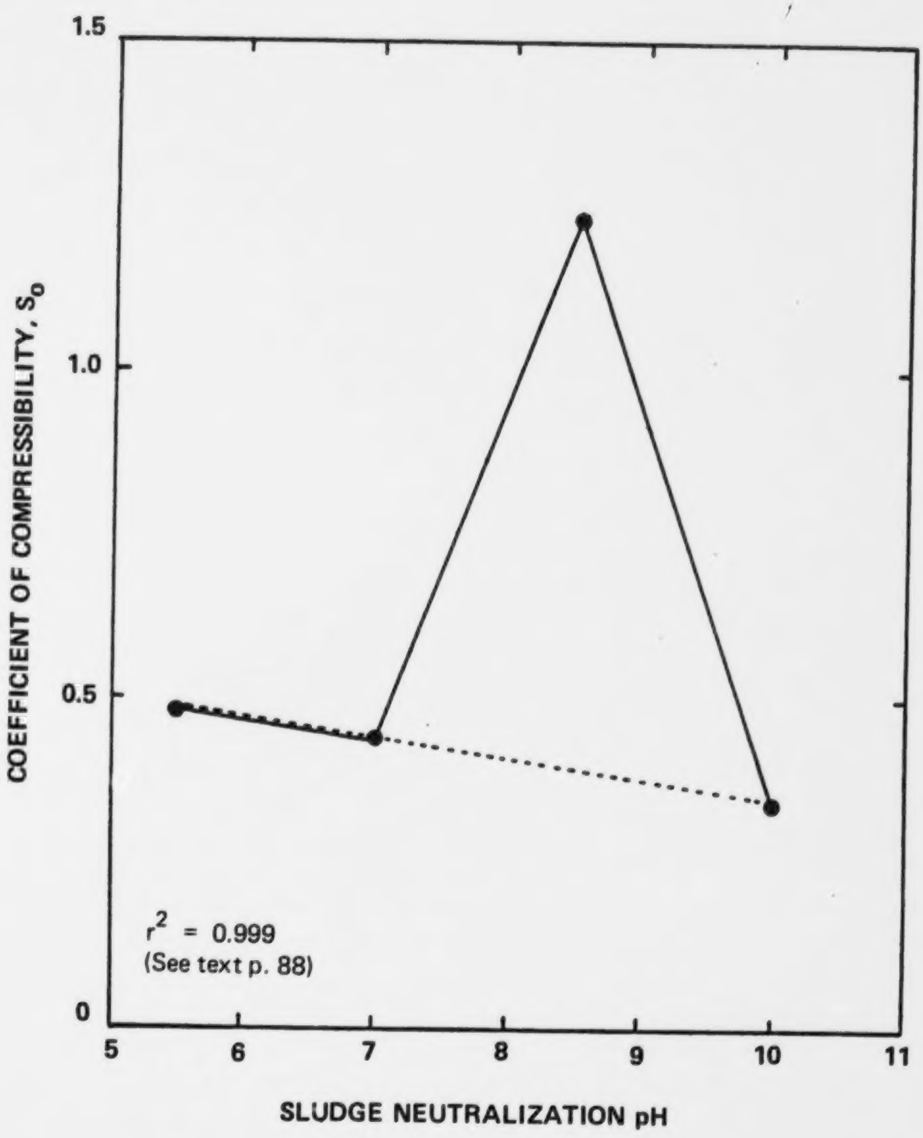

Figure 7.33. Effect of Sludge Neutralization pH on Sludge Compressibility Coefficients.

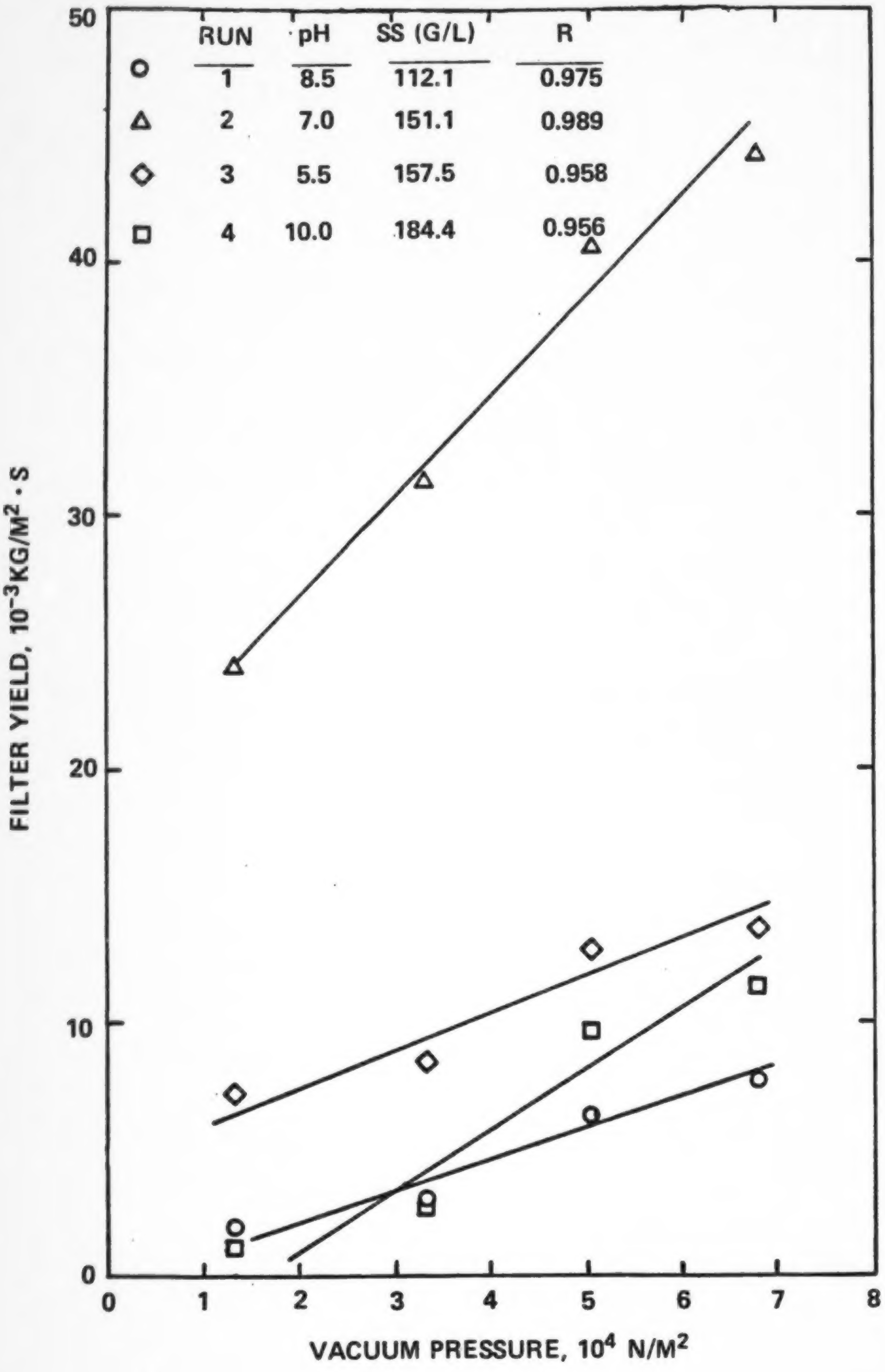

Figure 7.34. Effect of Vacuum Pressure on Filter Yield at Various pH Values.

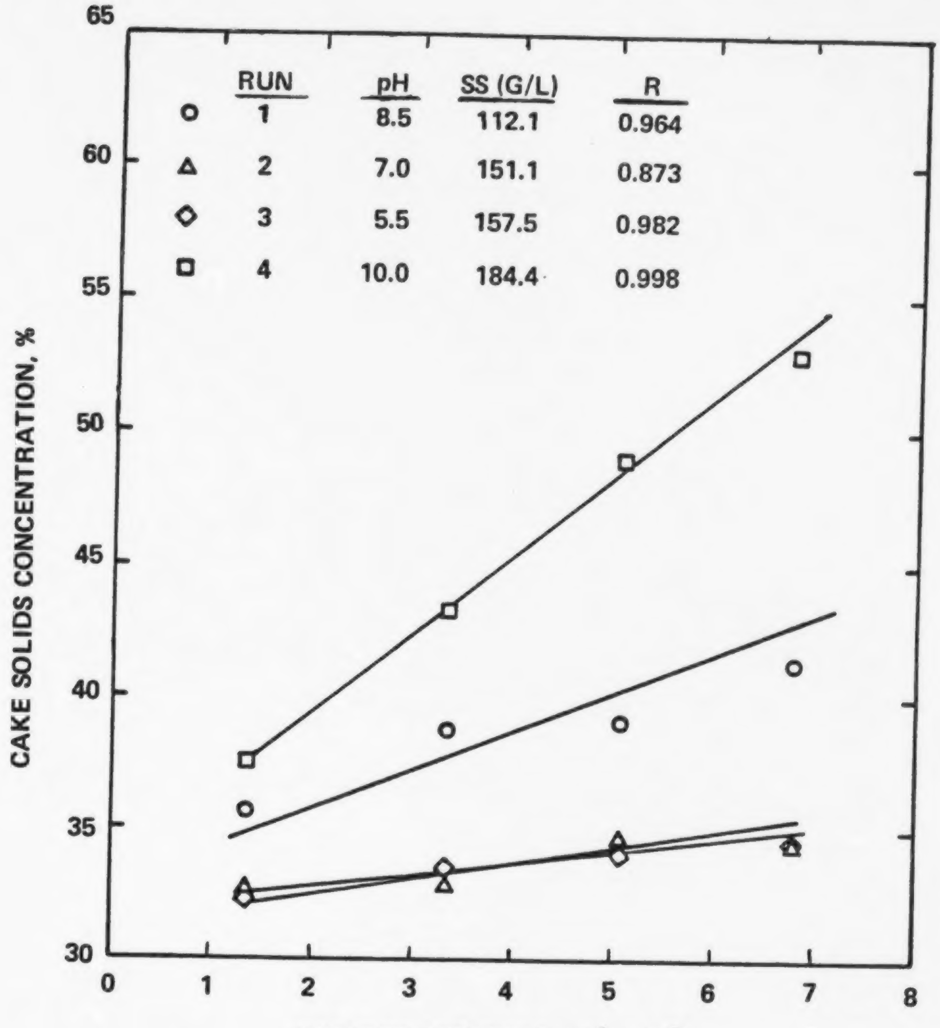

Figure 7.35. Effect of Applied Vacuum on Cake Solids Concentration.

Summary--

To evaluate the impact of segregated neutralization of spent etch and anodize solutions on sludge dewatering characteristics, data in Table 7.14 are presented. Since the concentrated finishing solutions were obtained from plant A3, data for sludges produced by conventional neutralization at plant A3 are included for comparison purposes. A suspended solids concentration of 35 g/l was arbitrarily selected to compare filter yield and CST values of segregated neutralization sludges with corresponding values at 36.1 g/l for conventional sludge from plant A3 which was produced at a pH of 7.0 and at room temperature. This was required since, unlike specific resistance values, filter yield and CST Measurements are not normalized to initial suspended solids concentration.

Definite improvements in sludge dewatering characteristics were apparent with segregated neutralization of spent finishing solutions at plant A3. Specific resistance values for conventional neutralization were greater than those observed for the sludges neutralized at 80°C. It was also apparent that an approximate 100-fold reduction in specific resistance could be achieved by the application of segregated neutralization of spent etch and anodize wastes at plant A3 at 80°C and a pH of 8.5. Segregated neutralization made dewatered sludge more amenable to disposal by decreasing sludge moisture content since all sludges produced at 80°C had higher cake solids contents after dewatering than those for conventional neutralization. For example, sludge produced at pH of 8.5 and a temperature of 80°C was dewatered to a concentration of 42.2 percent solids as compared to a concentration of 9.2 percent solids observed for the conventional sludge from plant A3, indicating that a reduction of about 36 percent in sludge cake moisture can be achieved by the application of segregated neutralization.

To further illustrate the impact of segregated neutralization on sludge dewatering characteristics, data illustrating vacuum-filter surface areas required to dewater each of the segregated neutralization and conventional neutralization sludges are presented in Table 7.15. Total masses of wet dewatered sludges for disposal are also presented. The values presented in Table 7.15 are based upon a total waste-aluminum mass-flow of 938 kg/d, which was estimated to be that treated by segregated neutralization of spent etch and anodize wastewaters at plant A3 from an industrial waste survey (Saunders _et al_., 1982). This mass of aluminum was assumed to be totally precipitated as aluminum hydroxide as a result of waste neutralization and was assumed to be totally removed by settling as a thickened sludge of 15 percent solids (150 g/l) for the sludges produced using segregated neutralization. Also, a 6-hour shift of vacuum filter operation was assumed for sludge dewatering in these calculations. Finally, filter yield and cake solids concentration values for conventional sludge in Table 7.14 were the highest values observed for these sludges (Saunders _et al_., 1982).

The results presented in Table 7.15 clearly demonstrated the significant impact of segregated neutralization on sludge treatment and disposal at the reference plant. A significant reduction in required vacuum-filter area can be achieved with this technique. As shown in the table for all the segregated neutralization sludges, a lower surface area was required for dewatering by vacuum filtration than that required to dewater conventional sludge. For sludge produced at a temperature of 80°C and a pH of 8.5, a filter area of approximately 3.7 m^2 was required to dewater segregated-neutralization sludge, as compared to the filter area of 22 m^2 required to dewater the conventional sludge. In addition, application of segregated neutralization results in production of sludge which can be dewatered to a higher solids content, thereby reducing the volume of wet sludge for disposal. A mass reduction of 77 percent was achieved by laboratory simulation of segregated neutralization at a

Table 7.14. Impact of Segregated Neutralization of Spent Process Solutions on Sludge Dewatering Characteristics

Neutralization Conditions		Specific Resistance		Filter Yield			CST	
pH	Temperature °C	SS* g/l	r 10^{10}m/kg	SS* g/l	Y** kg/m^2·h	Cake Solids percent	SS* g/l	CST s
SEGREGATED NEUTRALIZATION								
5.5	80	12.8 - 157.5	22.5 - 31.0	35.0	2.8	34.0	35.0	63.0
7.0	80	16.4 - 151.1	2.33 - 3.18	35.0	9.6	34.6	35.0	25.0
8.5[1]	80	20.8 - 157.8	1.33 - 2.95	35.0	6.2	42.2	35.0	25.0
10.0	80	25.4 - 256.3	0.34 - 0.87	35.0	0.78	52.8	35.0	25.0
CONVENTIONAL NEUTRALIZATION								
7.0[2]	25	3.4 - 36.1	28 - 38	3.4-36.1	0.70-5.71	8.5-9.2	3.4-36.1	18.1-53.7

*SS = suspended solids concentration

**approximate values from Figures 7.10, 7.13, 7.17 and 7.21

[1] Filter yield data from run 5

[2] Conventional sludge data from Saunders _et al_. (1982) for plant A3.

Table 7.15. Impact of a Segregated Neutralization of Spent Process Wastes at Plant A3 on Required Vacuum Filter Area and Mass of Wet Sludge for Disposal

Neutralization		Filter Yield	Cake Solids	Vacuum Filter Area	Mass of Wet Sludge for Disposal
pH	Temperature °C	kg/m²·h	percent	m²	kg/d
SEGREGATED NEUTRALIZATION					
5.5	80	39.6	34.2	11.4	7,925
7.0	80	144	34.8	3.1	7,790
8.5	80	122.4	40.0	3.7	6,775
10.0	80	21.6	46.7	20.9	5,800
CONVENTIONAL NEUTRALIZATION					
7.0	25	20.6	9.2	22.0	29,460

pH of 8.5 and a temperature of 80°C.

Therefore, use of segregated neutralization results in significant reductions in vacuum-filter area requirements, decreased quantities of wet sludge for disposal and an improved sludge-handling characteristics. Also, by storage of concentrated spent etch and anodize wastes for treatment when plant production is reduced, significant reductions in loading of conventional sludges to thickening and dewatering equipment will be achieved on days in which wastes are treated by conventional means, since approximately 75 percent of total waste aluminum can be treated by segregated neutralization of these concentrated spent solutions (Saunders et al., 1982). The potential for implementation of segregated neutralization at plant A3 and other similar plants was therefore established by the above analysis.

SUMMARY AND ENGINEERING SIGNIFICANCE

Thickening and dewatering properties of aluminum-finishing sludges are influenced by many factors including suspension temperature, age of the suspension and type of aluminum hydroxide formed upon neutralization of the waste. Temperature may affect suspension characteristics through the influence of liquid viscosity. Liquid viscosity affects particle drag forces during thickening and dewatering. With respect to thickening, at high suspended solids concentrations, interparticle forces predominate. Therefore, as suspended solids concentrations decrease, changes in analysis temperature would result in diverging settling curves obtained at different temperatures. Such a divergent relationship did not occur for the sludge thickening data obtained at the temperatures examined. Therefore, it may be concluded that under the conditions of this study, liquid viscosity did not appreciably influence the thickening data obtained for the sludges examined.

The majority of the dewatering data were collected at 25°C for sludges produced at a neutralization temperature of 80°C. Comparison of dewatering data collected 25°C and 80°C (Medero, 1981) indicated that temperature effects were incorporated into calculations of specific resistance through inclusion of filtrate viscosity but not with filter yield and CST values. However, the physical and chemical characteristics of segregated neutralization were not significantly affected by variations in suspension temperature.

The effects of chemical structure and aging on sludge properties are dependant on the chemistry of aluminum hydroxide formation during neutralization. Depending upon pH and temperature, numerous forms of aluminum precipitates are formed including, for example, amorphous, pseudoboehmite and trihydroxide forms. Amorphous aluminum precipitates (i.e., aluminum hydroxide preparations which are X-ray inactive and contain numerous trihydroxide and oxide-hydroxide forms) are hydrophilic, amphoteric forms with low crystalline order (Papee and Tertian, 1963: Maczura et al., 1978). Precipitation of aluminum at pH values below 7 results in formation of these amorphous forms which contain high levels of contaminant anions (e.g., $SO_4^=$, Cl^-) and have an average water content of 3 moles H_2O/mole Al_2O_3 (Maczura et al., 1979). In addition, Herbillion and Gastuche (1970) indicated that only amorphous and pseudoboehmite would be formed in the presence of high concentrations of chloride, nitrate and sulfate anions, regardless of pH. At high concentrations, the amorphous forms are easily coagulated into gels which upon aging may be converted into various trihydroxide forms. It is apparent from the properties of sludges formed by conventional neutralization at aluminum-finishing plants that amorphous forms are the predominate aluminum species precipitated and that the poor thickening and dewatering properties are attributable to the gelatinous nature of the precipitates.

With regard to trihydroxide forms, it is reported that at room temperature gibbsite is formed in acidic solution, nordstrandite is formed in slightly acid to neutral solution and bayerite is formed in alkaline solution (Barnhisel and Rich, 1965; Hsu, 1966; Hem and Roberson, 1967; and Schoen and Roberson, 1970). Herbillon and Gastuche (1970) observed that following removal of contaminant anions from aluminum solutions by dialysis, gibbsite precipitation occurred at pH 4.6 while precipitation of mixed bayerite and pseudoboehmite occurred at pH 6.5. In addition, mixed gibbsite and bayerite were formed at pH 8. Hayden and Rubin (1974) indicated that upon heating an aluminum nitrate solution for 5 days at 65°C and at low pH values (i.e., initial pH = 5.5; final pH = 4.1), gibbsite was formed. However, when the final pH was 4.42 (initial pH = 5.5), amorphous aluminum hydroxide was formed and pseudoboehmite was observed at a final pH of 7.25.

Papee and Tertian (1963) reported that, while amorphous forms were precipitated at pH values below 7, a gel-type boehmite (pseudoboehmite) was formed at pH 9 which had a lower water content (i.e., 1.5 - 2 mole H_2O/mole Al_2O_3) than amorphous forms. At pH values greater than 10, finely crystallized hyrates (e.g., nonstrandite and gibbsite) were also formed. In addition, the crystalline trihydroxide forms typically had lower water contents than the amorphous forms, as indicated in Table 7.16. Therefore, precipitation of non-amorphous trihydroxide forms would result in production of a suspension composed of crystalline solids with a water content less than that of amorphous sludge conventionally produced.

Table 7.16. Physical Characteristics of Selected Aluminum Precipitates

Aluminum Precipitate	Initial Water Content at Room Temperature: Mole H_2O / Mole Al_2O_3	Reference	Density* g/cm^3
Amorphous	3	1	-
	4	2	
Gibbsite	3	3	2.42
	2.5-3	1	
Bayerite	3.15	3	2.53
	2.5-3	1	
Nordstrandite	2.5-3	1	-
Boehmite	1.5-2	1	3.01
	1.15		
	1.5		

References: 1. Popee and Tertian, 1963; 2. Wefers and Bell, 1972;
3. Newsome *et al*., 1960
*Maczura *et al*., 1978

It is apparent that both neutralization pH and temperature greatly affect the chemical composition of neutralized aluminum suspensions. Increased temperature tends to reduce the overall water content of aluminum precipitates while increased pH values result in the formation of more crystalline forms, which also have lower water content values. In view of the high sulfate content of neutralized wastes examined herein, it is apparent that amorphous forms of aluminum hydroxide were precipitated during high temperature experimental runs, especially at a pH of 5.5. As pH was increased to neutral and alkaline values, crystalline aluminum trihydroxide and aluminum oxide hydroxide forms were apparently produced which tended to increase sludge density and decrease sludge water content (Hsu, 1967).

Aluminum suspensions produced at temperatures ranging from 65 to 90°C and at neutral pH values for thickening analyses were apparently composed of similar aluminum forms. That is, variations in neutralization temperature of up to 25°C did not significantly affect thickening properties. Changes in pH, however, had a dramatic effect on both thickening and dewatering properties. Sludges produced at increasing pH values appeared to contain an increased proportion of crystalline-like precipitates, apparently crystalline trihydroxide forms, which accounted for the enhancement of thickening and dewatering properties. However, regardless of mechanism, segregated neutralization of concentrated aluminum-finishing wastes results in major improvements in the performance of sludge treatment systems and has a major impact on reduction of the volume of sludge for disposal due to decreases in sludge mositure content.

As to implementation of segregated neutralization there are a number of possible approaches. A completely separate system could be implemented with two sedimentation and dewatering systems provided to treat sludges produced by conventional neutralization and segregated neutralization. This alternative should be successful but would be cost intensive due to the requirements for redundant thickening and dewatering systems. Data presented by Saunders et al. (1982) for an anodizing plant (plant A2) employing a version of segregated neutralization indicates that other options are available. At plant A2, only rinsewaters are treated by neutralization and sedimentation in a solids-contact clarifier during periods when aluminum is actively being finished, usually 5 or 6 days/week. On a day when aluminum is not being finished, concentrated finishing solutions are discharged to the neutralization system resulting in major increases in suspension temperature. Massive quantities of waste solids are precipitated and stored in the solids-contact clarifier for dewatering during a period of normal plant operation. Examination of the sludge produced during this latter period when "segregated neutralization" was being practiced indicated that the sludge had superior thickening and dewatering properties when comapred to those produced conventionally. In addition, using a vacuum filter for dewatering the combined sludge solids at the plant site, cake solids contents of 20 percent and higher are routinely achieved. No other plant investigated by Saunders et al. (1982) was able to achieve this level of dewatering. Therefore, it would appear that the improved thickening and dewatering properties of sludges produced by segregated neutralization can be used to improve the properties of conventional sludges by mixing the two together. Neutralization of concentrated finishing solutions would be conducted with a segregated system, with the effluent solids being mixed with dilute rinsewater wastes prior to or following conventional neutralization for further treatment. Segregated neutralization solids could also be blended with conventional sludge following thickening but prior to dewatering the mixture. Experimental results indicate that these alternatives are feasible. Further investigation is, however, required to confirm the benefits of these and other alternatives as well as establish the optimal alternative.

SECTION 8

RECLAMATION OF SPENT CAUSTIC ETCH BY LIME ADDITION

The major source of waste aluminum from an aluminum anodizing plant is spent caustic etch. Studies conducted at plants A1 and A3 indicated that 73 and 59 percent of total waste aluminum was continued in spent etch, respectively. In addition, aluminum in spent etch is in a concentrated form since, for example, spent etch accounted for only 1.2 and 1.5 percent of the total wastewater flow at plants A1 and A3, respectively. Treatment of the major portion of a waste contaminant in a concentrated form provides an excellent opportunity to reduce waste treatment costs.

New technology presented by Alcoa, Inc. and Fugi Sash, Inc. provides a means of removing aluminum as a low-moisture aluminum-hydrate precipitate and recovering caustic etch for the use in the finishing process (Brown, 1982; Meyer et al., 1979). Caustic etching solutions are continuously or periodically circulated through a crystallizer containing aluminum-hydrate crystals and aluminum is precipitated and removed from suspension by gravity sedimentation. Clarified etch is reused in the etching process while the aluminum-hydrate suspension is periodically dewatered to recover precipitated aluminum-hydrate solids. These proprietary etch-recovery systems have found favorable application in the aluminum finishing industry.

Data presented by Schaezler (1978), Kelly (1960) and Holmes (1982) indicated a limited solubility for aluminum in presence of calcium ions at elevated pH values. At sufficient calcium levels, aluminum is virtually insoluble as a calcium aluminate (Schaezler, 1978; Holmes, 1982), unlike the proprietary etch recovery systems in which soluble aluminum levels in recovered etch solutions remains between 16 and 24 g/l (Brown, 1982). In addition, the process of calcium addition is not proprietary in nature, and appears to be simpler technology with potential for application in the aluminum finishing industry. Therefore, initial studies were conducted to determine the feasibility of the process with respect to waste treatment considerations.

EXPERIMENTAL TECHNIQUES

Experimental Reactor System

All experimental studies were conducted in one-litre glass beakers which were mixed with a single-blade (7.7cm x 2.4 cm) stainless-steel paddle at 100 rpm. Constant temperatures were maintained by placing reaction beakers (up to a maximum of five) in a constant-temperature bath.

Individual experiments were conducted by placing 200 ml of a spent caustic solution in a beaker and weighing the beaker and caustic solution (to the nearest 0.1g). The beaker was allowed to equilibrate for 10 minutes in the constant-temperature bath. Lime (reagent-grade hydrated lime, $Ca(OH)_2$) was then added to the spent etch solution as a dry powder over a 90-second interval and the reaction was allowed to proceed for reaction periods of 15 minutes to 10 hours. At the end of each reaction period, individual beakers were removed from the constant-temperature bath, towel dried and weighed to determine the net evaporation loss. At reaction temperatures at and above 60°C, evaporation losses were corrected by addition of distilled, deionized water to each beaker. Water addition was accomplished by pipetting 3.5 ml of preheated water into a beaker at 30-minute intervals. At completion of an experiment, no additional water was added but initial and final reactor weights were used to compute a dilution factor which was used in correcting subsequent analytical data.

Following completion of a specified reaction period, the entire contents of a beaker were filtered on a Buchner funnel apparatus to determine specific resistance, solids yield, cake volume, and filtrate characteristics. Filtrate was passed through a 0.45 µm membrane filter prior to analysis for residual soluble calcium and aluminum, pH, dissolved solids and alkalinity.

Spent Etch Waste

Spent etch from plant A3 was collected from a spacer-etch tank for use in the study. The spacer-etch tank received spent etch from the anodize line and was used to clean spacers used on aluminum racks. The contents of the spacer-etch tank were continually discharged to a holding tank for use in neutralization of plant wastewaters.

Characteristics of the spent etch solution used in the study are presented in Table 8.1. The majority of the aluminum in the sample was in the dissolved form as were the majority of the solids contained in the etch solution. The characteristics of the etch solution were in addition similar to those presented by others (Brown, 1982; Ramirez, 1979; Saunders et al., 1982) for spent caustic etch solutions.

EXPERIMENTAL RESULTS

In examination of the use of lime addition for reclamation of spent caustic etch, primary attention was placed on required reaction time and calcium levels to achieve aluminum removal and on characteristics of precipitated solids following lime addition.

Reaction Time

Initial duplicate tests with reaction times varying from 45 to 90 minutes failed to produce consistent results. Subsequent investigations into the effects of reaction time and temperature revealed that both had significant impact on aluminum removal, as indicated in Figure 8.1.

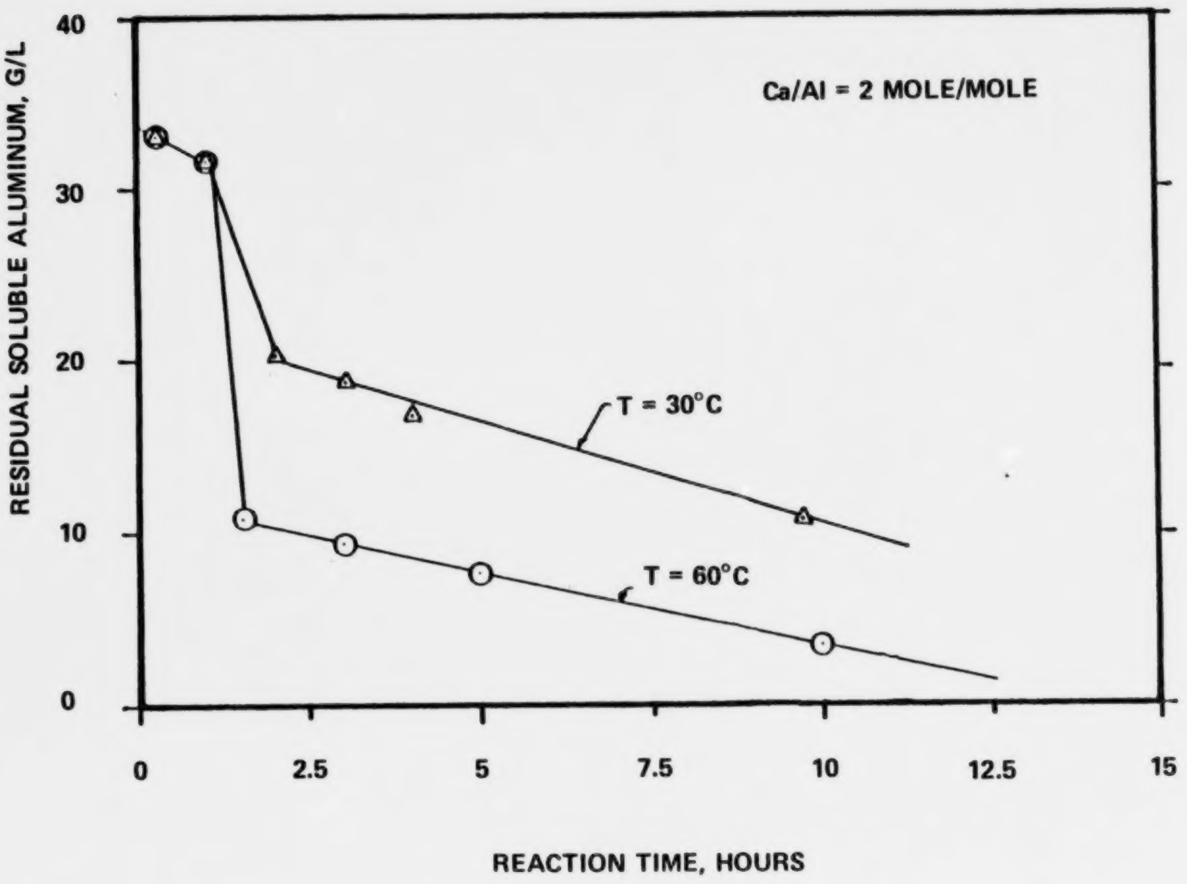

Figure 8.1. Relationship Between Residual Soluble Aluminum and Reaction Time at a Constant Ca/Al Molar Ratio of 2/1.

Table 8.1 Characteristics of Spent Etch Waste From Plant A3 as Used in Experimental Investigation

PARAMETER	CONCENTRATION
Solids	
Total, g/l.	190.4
Dissolved, g/l.	189.3
Solution Density, kg/l.	1.15
pH.	13.6
Alkalinity, g/l (as $CaCO_3$).	15.6
Aluminum	
Total, g/l.	37.5
Dissolved, g/l.	36.5
Calcium, mg/l.	1

Data in Figure 8.1 indicated that no significant aluminum precipitation occurred in an initial 45-minute period at temperatures of 30 and 60°C for a mass dosage of Ca/Al=3/1. However, following reaction periods of between 45 and 90 minutes, rapid aluminum precipitation occurred. For a reaction temperature of 60°C, the total aluminum removal following a 90-minute reaction period was 68 percent while at a reaction temperature of 30°C, aluminum removal was 45 percent. After a 90-minute reaction period, the rate of aluminum precipitation decreased and remained constant through a 10-hour period at both temperatures. The approximate rates of aluminum precipitation for 30 and 60°C were 1.2 g/l·h and 0.75 g/l·h, respectively, over the reaction time period of 1.5 to 10 hours.

Since process performance was affected by both reaction time and temperature, it was necessary to establish a constant value for one of the parameters to remain within realistic experimentation limits. A reaction time of 6 hours was therefore chosen for all subsequent experiments. A 6-hour reaction period was considered reasonable for a full-scale system and would assure process stability. Data presented in Figure 8.1 indicated that for reaction times greater than 90 minutes, changes in residual aluminum were slight compared to those for reaction times of 90 minutes or less. Therefore, the low rate of change allowed for consistant duplication of experimental results when using reaction times of 6 hours.

Reaction Stoichiometry

Using a reaction time of 6 hours following lime addition, a series of studies were conducted at ambient temperature (25°C) and 60°C, with 60°C being typical of that used for etching solutions on aluminum anodizing lines. Incremental increases in calcium addition were used to determine the effect on residual aluminum. As indicated in Figure 8.2, increased addition of lime resulted in a proportional decrease in residual soluble aluminum, indicating a constant relationship between lime (i.e., calcium) addition and aluminum removal. Furthermore, residual soluble calcium in filtrate samples following a 6-hour reaction period remained between 1 to 5 mg/l at calcium to aluminum molar ratios of 1 to 5. Calcium therefore reacted with aluminum or other species to form precipitates and was only slightly soluble in the etch solution.

Extrapolation of data in Figure 8.2 to zero residual aluminum indicated that the required molar ratios of calcium to aluminum were 2.75/1 and 3.7/1 for 60°C and 25°C, respectively. The respective mass ratios for 60°C and 25°C were 4.1/1 and 5.4/1. Lime requirements at ambient temperature (i.e., 25°C) were 34 percent higher than those at 60°C for the 6-hour reaction period examined. This was consistent with data in Figure 8.1 which indicated, however, that similar aluminum removals could be achieved at two temperatures using a constant Ca/Al ratio if reaction time was extended at the lower temperature.

With respect to filtrate quality for experiments conducted at calcium to aluminum molar ratios ranging from 1 to 3 at 25 and 60°C, alkalinity and pH values remained constant. Dissolved solids, however, decreased with increasing calcium addition due to removal of soluble aluminum. In Figure 8.3, residual dissolved solids concentration is presented as a function of residual soluble aluminum for a reaction temperature of 30°C at various calcium to aluminum ratios. The removal of 1g of aluminum by addition of lime resulted in a net reduction in dissolved solids of 1.25g. Residual dissolved solids concentration following removal of all aluminum was 147 g/l, which was attributable to sodium hydroxide and etch additives. Therefore, complete removal of aluminum by lime addition could be successfully achieved without a reduction in the strength of the etching solution, as indicated by alkalinity and dissolved solids levels.

The quantity of sludge solids produced by addition of lime was examined by analysis of the quantities of calcium and aluminum added. For a given Ca/Al ratio, initial and final aluminum and calcium concentrations of a treated etch solution were used to determine the quantity of calcium and aluminum removed as precipitated solids. These calculated values are compared with measured values for cake solids in Figure 8.4. For a range of Ca/Al ratios, calcium and aluminum accounted for approximately 46 percent of the dry solids produced. Other cations and associated anions were obviously precipitated with calcium and aluminum.

Sludge Characteristics

Addition of lime to spent etch produced a suspension which contained a high concentration of suspended solids resulting from the precipitation of calcium and aluminum. Initial investigation indicated that the suspensions were directly amenable to dewatering and that initial thickening was not required. Analyses of sludge characteristics were therefore focused on measures of sludge dewatering properties.

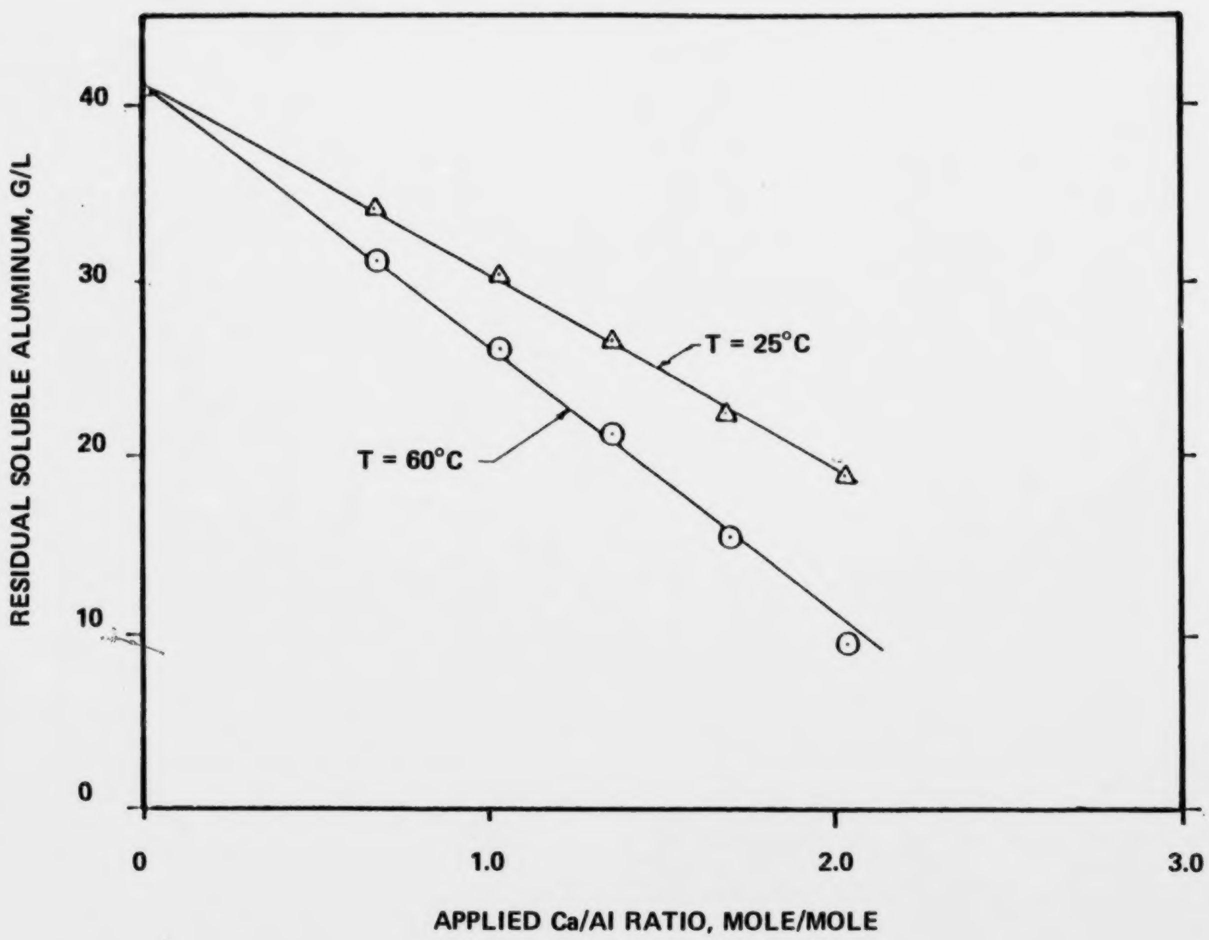

Figure 8.2. Relationship Between Residual Soluble Aluminum and Applied Ca/Al Dose.

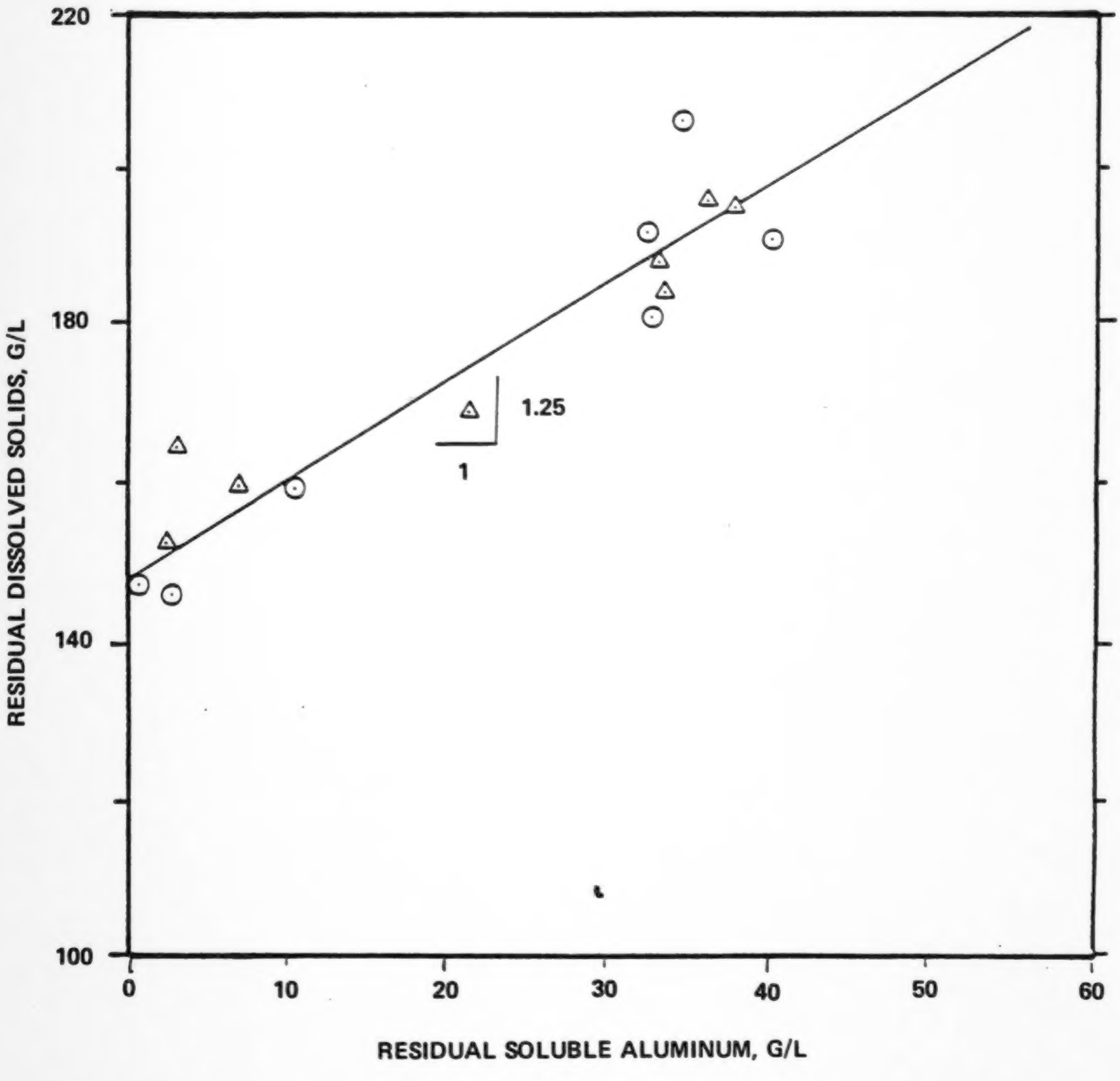

Figure 8.3. Relationship Between Residual Dissolved Solids and Residual Soluble Aluminum for Various Ca/Al Ratios and a Reaction Temperature of 30°C.

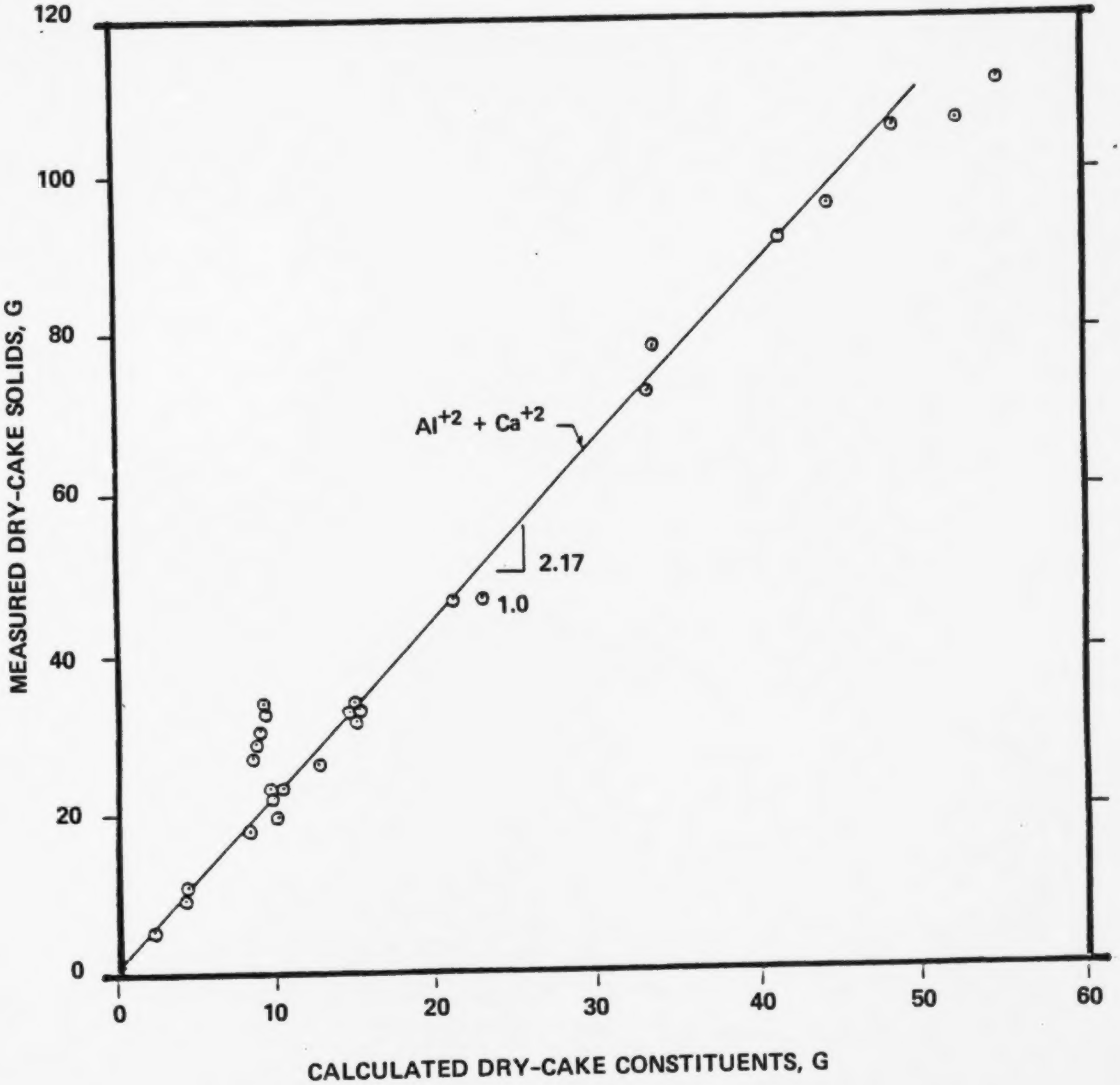

Figure 8.4. Relationship Between Measured Dry-Cake Solids and Corresponding Aluminum and Calcium Composition as Calculated from Initial and Final Concentrations in Treated Etch.

Specific Resistance--

To examine sludge dewatering characteristics, numerous experiments were conducted at temperatures of 25, 43 and 60^oC and applied calcium to aluminum mass ratios of 1 to 3. Visual observations made during these experiments indicated that the sludges typically had a coarse-grain texture similar to that for wet sand for reaction temperatures of 25^oC and a smoother texture as reaction temperatures were increased to 43 and 60^oC. In general, sludges produced at lower temperatures and Ca/Al ratios had poor cake-release characteristics during testing for specific resistance, while those produced at higher temperatures and Ca/Al ratios exhibited excellent cake-release characteristics. Sludges produced at low temperatures and Ca/Al ratios retained the green color which was characteristic of the original spent etch solution while those produced at increasing temperatures and high Ca/Al ratios had an off-white color. In addition to these general sludge characteristics, specific resistance measurements were used to evaluate the effects of reaction time, Ca/Al ratio and reaction temperature.

Reaction Time-- Owing to color and texture changes noted for increased reaction temperatures, it was suspected that specific resistance varied with reaction time. Specific resistance results at various reaction times are presented in Figure 8.5. Analysis of these data indicated that for a 25^oC reaction temperature, specific resistance was at a minimum and did not significantly change during the first 1.5 hours of reaction. For a reaction time of 1.5 to 6 hours, specific resistance increased by an order of magnitude, i.e., from 5×10^9 m/kg to 6×10^{10} m/kg. The resistance to dewatering being at a minimum during the initial 1.5-hour period corresponded to earlier data (Figure 8.1) indicating limited aluminum removal during this period.

For reaction times of 0.5 to 1.5 hours,specific resistance decreased from 5.7×10^{10} m/kg to 1.5×10^{10} m/kg at 60^oC. For reaction times of 1.5 to 6 hours, specific resistance increased from 1.5 to 10^{10} m/kg to a maximum of 6.1×10^{10} m/kg. In general, increased reaction time indicated that additional sludge solids were being produced (see Figure 8.1) and that the resistance of those solids to the passage of etch during mechanical dewatering increased for a reaction temperature of 25^oC and remained relatively constant at 60^oC (see Figure 8.5).

Calcium to Aluminum Ratio-- To evaluate the effects of calcium to aluminum ratio on sludge dewatering properties, a constant reaction time of 6 hours was employed, as indicated previously. Specific resistance values obtained for the sludges produced at temperatures of 25, 43 and 60^oC ranged between 2.8×10^{10} m/kg and 47.5×10^{10} m/kg, as indicated in Table 8.2. These values were approximately 10-fold less than those obtained by Saunders et al. (1982) for unconditional aluminum-finishing sludges produced by conventional neutralization (e.g., $1.8 - 51 \times 10^{11}$ m/kg), indicating improved dewatering properties over conventional aluminum-finishing sludges. In addition, the values reported in Table 8.2 are based on viscosity values for water at the temperature of the experiment. The viscosity of the spent etch solution was, however, higher than that for water but was not measured for inclusion in the calculation. Therefore,

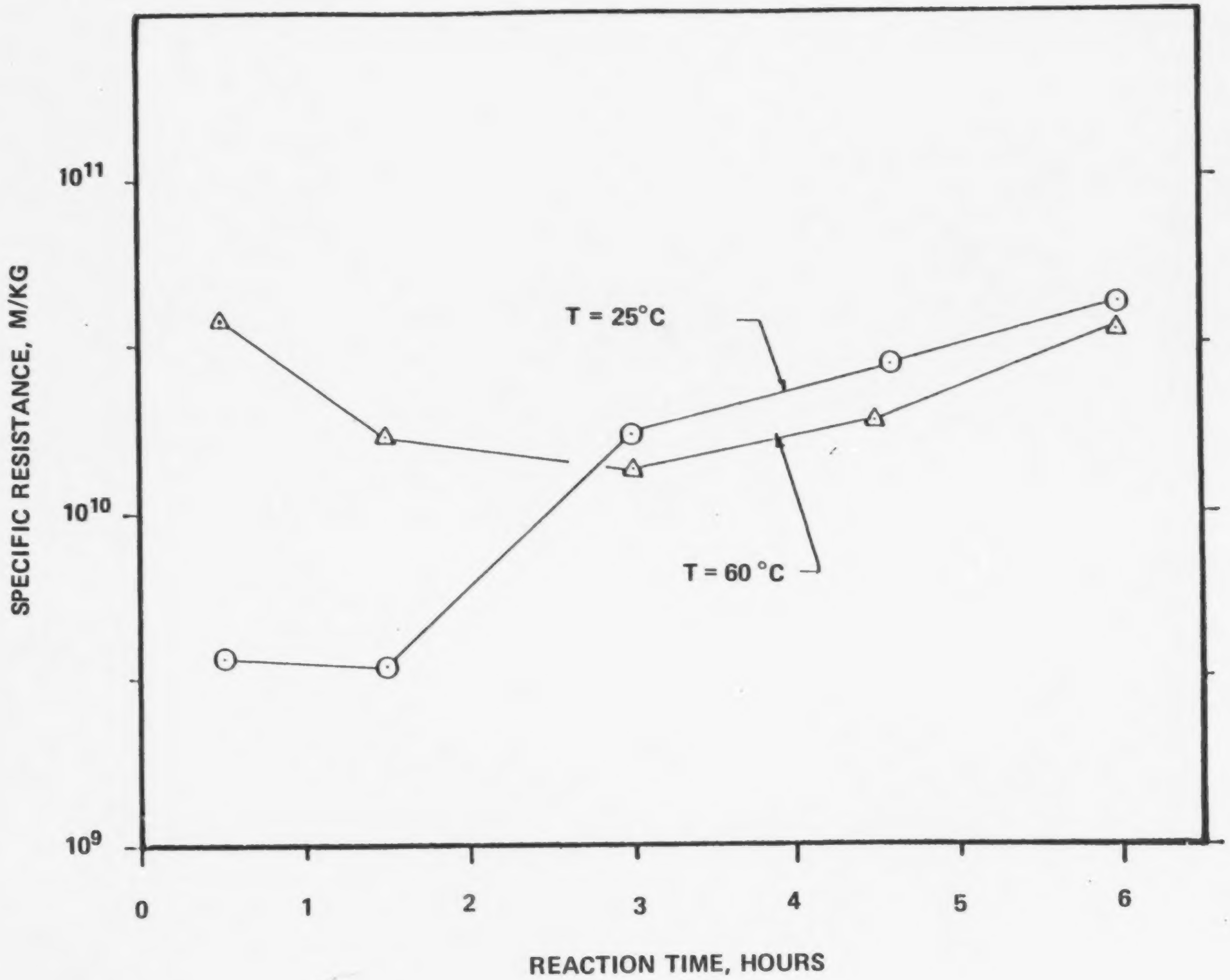

Figure 8.5. Relationship Between Specific Resistance and Reaction Time for Temperatures of 25°C and 60°C at Ca/Al of 3 g/g.

Table 8.2 Specific Resistance of Lime-Treated Spent Etch Sludges

Reaction Temperature °C	SPECIFIC RESISTANCE 10^{10} m/kg Applied Ca/Al Ratio (Mass basis)* 1.0	1.5	2.0	2.5	3.0
25	2.8	6.4	6.8	4.3	4.0
43	14.	9.6	6.4	5.2	5.6
60	47.5	8.4	5.0	4.0	5.4

* Ca/Al (molar basis) = [Ca/Al (mass basis)] x 0.675

the reported values should be further reduced by a factor equal to the ratio of the viscosity of water, μ_{H_2O}, to the viscosity of spent etch, μ_{NaOH}. For 2 to 8 percent etch solutions at temperatures of 25 to 60°C, the viscosity ratio is approximately 0.67, indicating that actual specific resistance values should be reduced by approximately one-third.

The effect of Ca/Al ratio at a reaction period of 6 hours on specific resistance is presented graphically in Figure 8.6. For reaction temperatures of 43°C and 60°C, the resistance to dewatering decreased with increased calcium dosages. For a reaction temperature of 25°C, the resistance to dewatering increased as the mass Ca/Al dosage increased from 1:1 to 1.5:1 but remained relatively constant for additional increases in the Ca/Al ratio. In addition, reaction temperature had a minor impact on specific resistance. Except for the value at a Ca/Al mass ratio of 1.0 at 25°C, specific resistance values in Figure 8.6 followed similar relationships at all temperatures.

Dewatered Cake Solids Content-- The relationships between applied Ca/Al ratio and solids content of dewatered cakes produced in specific resistance tests are shown in Figure 8.7 at reaction temperatures of 25°C and 60°C. Dry cake solids did not significantly change over the range of applied doses for each of the reaction temperatures. However, there was a significant difference between the solids content at reaction temperatures of 60°C and 25°C. The average dry solids content at a reaction temperature of 60°C was 52.5 percent while the average dry solids content at a reaction temperature of 25°C was 48 percent dry solids. Thus, for a reaction temperature of 60°C, approximately 8.5 percent less dewatered sludge mass resulted as compared to reaction temperatures of 25°C for equivalent Ca/Al dosage ratios.

Filter-Leaf Yield--

Results of filter leaf testing are shown in Figure 8.7. Due to limited quantities of sludge available for laboratory study and the quantity of sludge required for leaf testing, only limited testing was conducted. Data for three temperatures at a Ca/Al mass ratio of 3.5/1 are

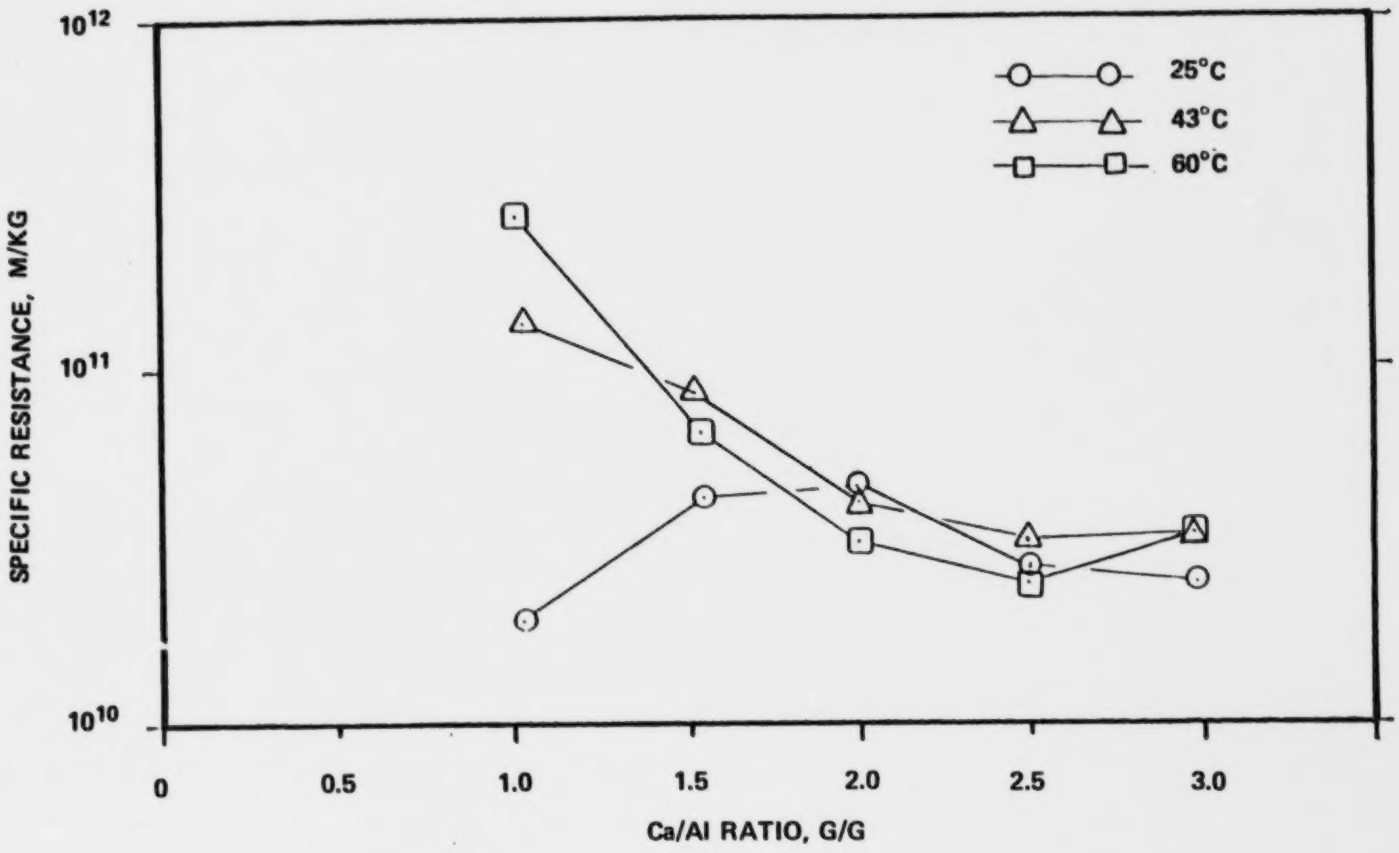

Figure 8.6. Relationship Between Specific Resistance and Applied Ca/Al Ratios for Reaction Temperatures of 25, 42 and 60°C.

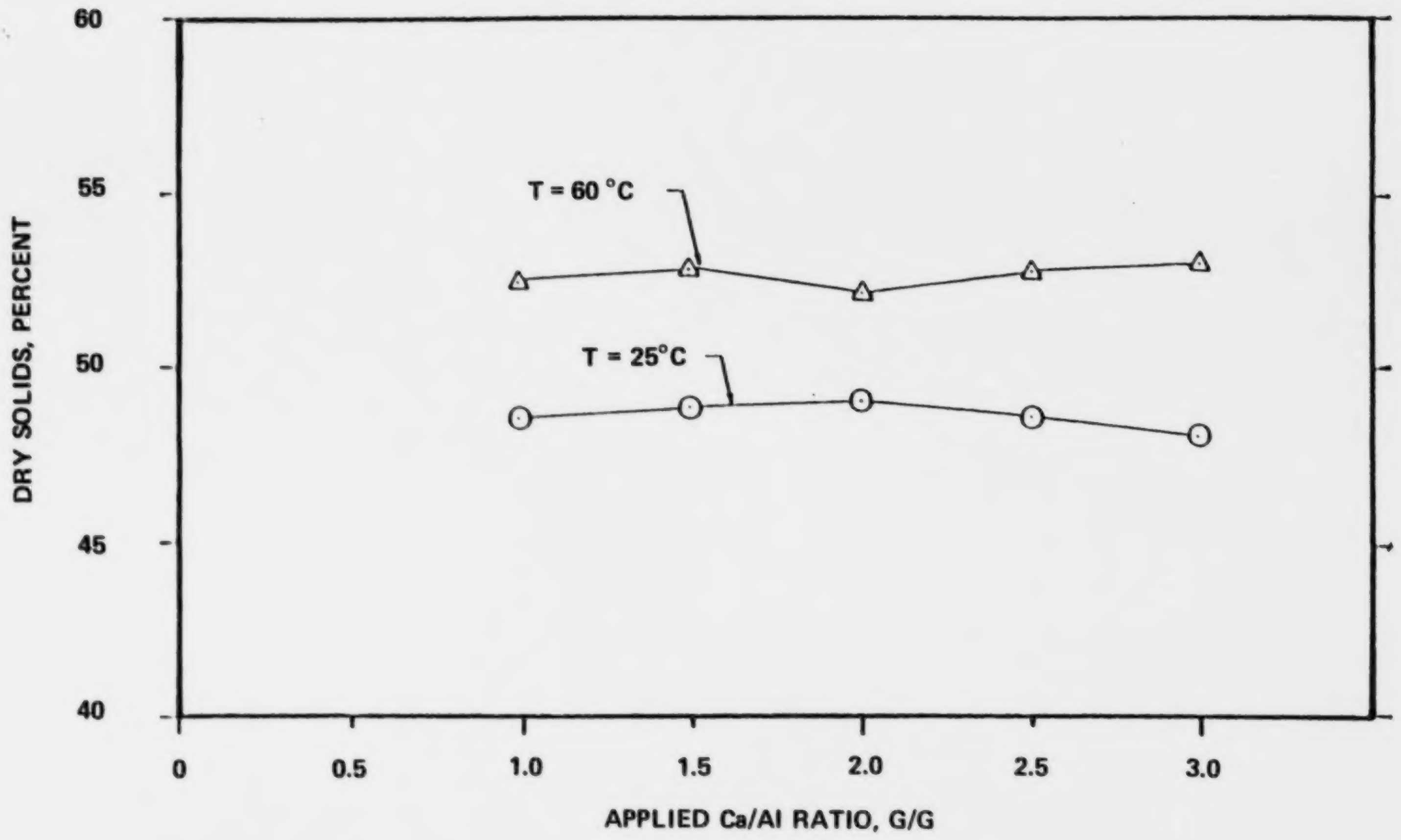

Figure 8.7. Relationship Between Applied Calcium to Aluminum Ratio and Dewatered Cakes Solids Content at Reaction Temperatures of 25 and 60°C.

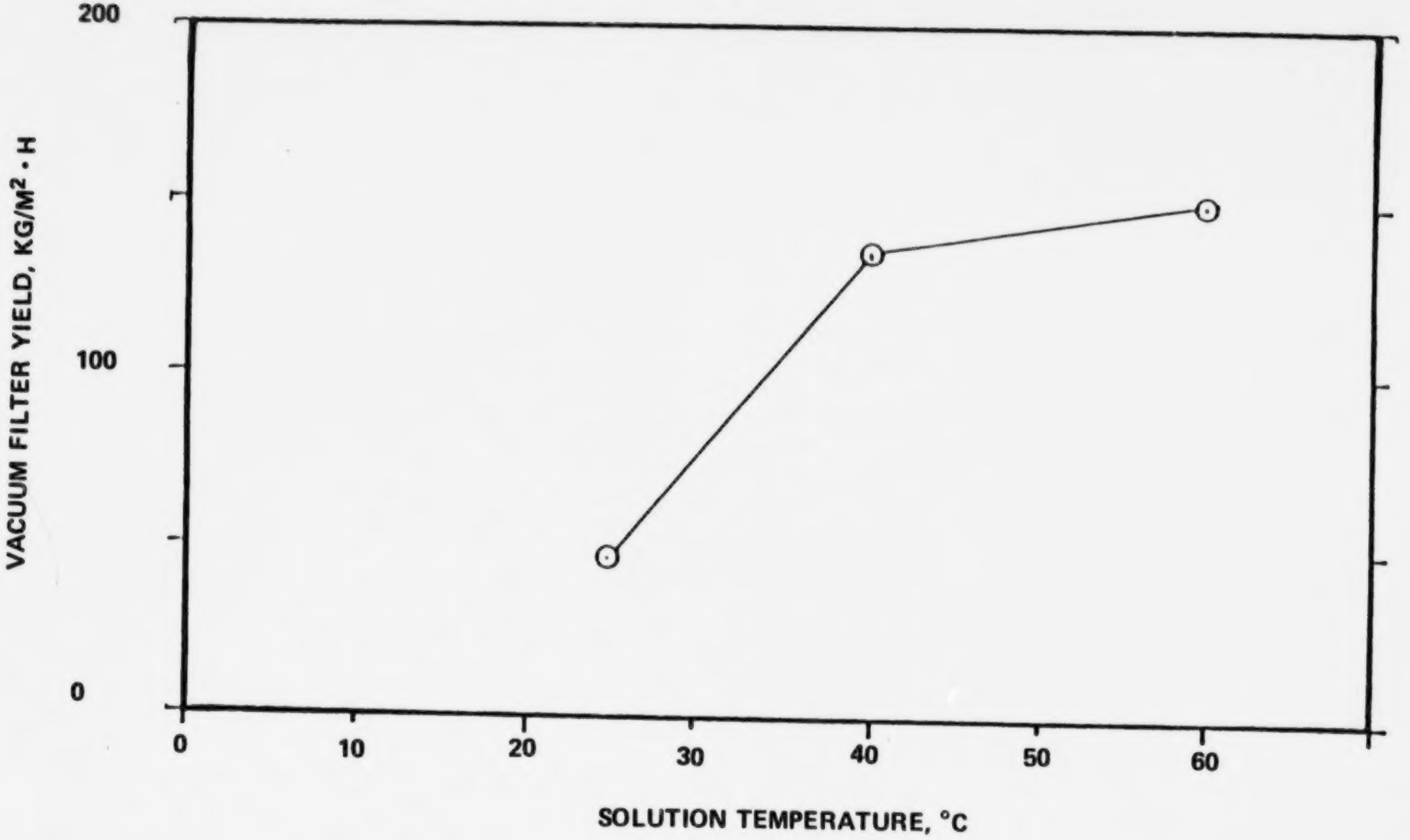

Figure 8.8. Relationship Between Vacuum Filter Yields and Solution Temperature for an Applied Ca/Al Mass Ratio of 2.5/1.

presented in Figure 8.8. Filter-leaf yields for 25, 43 and 60°C were 48.8, 133.3 and 146.4 $kg/m^2 \cdot h$, respectively. Cake release for the 25°C filtration temperature was poor and the cake had to be removed from the filter with a knife edge. At filtration temperatures of 45°C and 60°C, cakes self-discharged from the media with release of vacuum. Analysis of Figure 8.8 indicated that filter yields were drastically reduced at a sludge temperature of 25°C. In fact, the data indicated a 200 percent decrease in filter yield for a sludge filtration temperature of 25°C as opposed to filtration temperatures of 43 and 60°C.

DISCUSSION

Results of laboratory experiments indicated that reclamation of spent etch could be achieved by precipitation of aluminum with lime. Mechanical filtration of the suspension could be successfully employed to remove precipitated-aluminum solids and recover the caustic etch solution for reuse. Discussion of the results of the study are focused on reaction chemistry, sludge treatment and disposal and process application.

Reaction Chemistry

Addition of hydrated lime to a spent caustic etch solution resulted in the concurrent precipitation of aluminum and calcium at temperatures of 25 to 60°C. The principal cations in lime-treated etch solutions were aluminum, sodium and calcium followed by alloy-contaminant metals while principal anions were hydroxyl ions. At the extreme alkaline conditions of spent caustic etch wastes, the most probable chemical precipitates formed upon lime addition were calcium aluminates.

According to Kelly (1960), calcium forms four well-defined anhydrous aluminates and approximately ten hydrated aluminates. The four anhydrous forms are presented as $CaO \cdot Al_2O_3$; $3CaO \cdot Al_2O_3$; $3CaO \cdot 5Al_2O_3$; and $5CaO \cdot Al_2O_3$ (Kelly, 1960). The most well-known hydrated forms are $3CaO \cdot Al_2O_3 \cdot 6H_2O$; $2CaO \cdot Al_2O_3 \cdot 8H_2O$; $3CaO \cdot Al_2O_3 \cdot 12H_2O$; and $4CaO \cdot Al_2O_3 \cdot 12H_2O$, although $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is generally agreed to be the only stable aluminate at temperatures between 20 and 215°C (Kelly, 1960; Pepples and Wells, 1954; Carlson, 1958). In addition, Schaezler (1978) examined the chemistry of calcium aluminate formation in mineralized municipal waters and found precipitate composition to be represented by $3.4\,CaO \cdot Al_2O_3 \cdot 8.8H_2O$, $4.2CaO \cdot Al_2O_3 \cdot 13.2H_2O$ and $1.7\,CaO \cdot Al_2O_3 \cdot 5.7H_2O$ at initial calcium to aluminum ratios (molar) of 3, 4 and 2, respectively.

Calcium application rates, expressed as a molar ratio of calcium to aluminum, of 2.75 and 3.7 were required to remove aluminum from spent etch in a 6-hour period at temperatures of 60 and 25°C, respectively. These values were within the range of values presented by Schaezler (1978). Molar calcium to aluminum ratios for the calcium aluminates presented by Kelly (1960) ranged from 0.3 to 1.5 and 1 to 2 for anhydrous and hydrated forms, respectively. These values were lower than the levels of calcium applied relative to aluminum. Direct comparison of chemical composition data obtained herein to that presented by Kelly (1960) is, however, not possible. As indicated in Figure 8.1, equilibrium conditions were not reached within the reaction time of 6 hours used throughout the study and aluminum precipitation continued to occur at all calcium to aluminum ratios.

However, it is apparent that the results obtained are consistent with those presented by Schaezler (1978) for calcium to aluminum ratios and that the most probable chemical precipitates formed were hydrated calcium aluminates. Since non-equilibrium conditions were monitored throughout the study, it is impossible to predict the exact form of the aluminum precipitates.

Laboratory results indicated that the calcium aluminate reaction was enhanced by increases in reaction temperature and reaction time. Increases in temperature from 30^oC to 60^oC decreased the molar Ca/Al ratio from 4.5 to 2.75 for a reaction time of 6 hours. Thus, for equal amounts of aluminum in solution, a 30^oC increase in reaction temperature resulted in a 29 percent reduction in lime requirements. For a prototype unit, this reduction in raw chemical consumption would also result in a reduction in the mass of sludge for disposal and thus a reduction in ultimate sludge dewatering and disposal costs. Considering the beneficial effects of high reaction temperature on reaction stochiometry, scale-up of an etch recovery system should be designed for high temperatures. Since an etch tank used in finishing aluminum is maintained at temperatures of 55 to 65^oC, etch recovery systems could be effectively employed at these temperatures to minimize chemical requirements. As presented in Figure 8.1, longer reaction periods provided for more effective precipitation at a given lime application rate. However, the effect of increased reaction time on the temperature of the suspension must be considered when including this variable into the design of a prototype system.

Sludge Treatment and Disposal

Calcium aluminate sludges exhibited minimum specific resistance values and maximum values for cake solids contents at reaction temperatures of 60^oC and molar Ca/Al doses equal to or exceeding 2.0 at a reaction time of 6 hours. These sludges had characteristic specific resistance values of approximately 5.4×10^{10} m/kg and cake solids contents typically exceeding 52 percent. These data compare very favorably with conventional sludges produced at Plant A3 which have typical specific resistance values for unconditioned sludges ranging from 2.8 to 3.8×10^{11} m/kg and dry solids of 8 to 14 percent (Saunders et al., 1982). Calcium aluminate sludges produced in etch recovery had specific resistance values which were 10-fold lower than those for conventional sludges (when correcting for viscosity differences in calcium aluminate sludges) and dewatered to a dry solids content which was 3.7- to 6.5-fold higher than that for conventional sludges produced at the plant.

Reaction temperature increased the extent of aluminum precipitation at a given Ca/Al ratio but did not significantly affect sludge dewatering characteristics. As presented in Figure 8.6, specific resistance data were similar at virtually all Ca/Al values, although solids contents of dewatered cakes did increase with reaction temperature.

Limited filter leaf tests conducted at a reaction temperature of 60^oC and a molar Ca/Al ratio of 1.7 resulted in simulated vacuum-filter yields of 48.8 to 146.4 $kg/m^2 \cdot h$. Filter yields reported by Saunders et al. (1982) for unconditioned conventional sludges produced in aluminum-finishing plants ranged from 0.37 to 20.54 kg/$m^2 \cdot h$. The improved yields for calcium-aluminate sludges were attributable to increased initial suspended solids concentrations and to improved sludge dewatering properties.

Process Application and Engineering Significance

In consideration of application of the etch recovery process, it is assumed that an operational temperature of 60°C and reaction time of six hours are practical. For purposes of examination, the information in Section 6 are to be used in considering use of etch recovery on the anodize line at plant Al. With a spent etch production rate of 6.3m^3/d, a reaction vessel for lime addition with a volume of approximately 1.6m^3 would be required (e.g., diameter = 1m and depth = 3m (including 0.8m^3 of freeboard volume)). In addition, a lime addition system and vacuum filter would be required. The installation, therefore, would not be a major one and would occupy only a small portion of a plant site.

In consideration of the impact on sludge production, data presented in Section 6 indicated the total aluminum wastage rate at plant Al was 566 kg/d. To determine the impact of etch recovery on sludge production, it was assumed that this quantity of aluminum would be precipitated as $Al(OH)_3$ and dewatered to a solids content of 12 percent for normal operational conditions. For implementation of an etch recovery system using lime addition, it was assumed that all spent etch was removed as calcium aluminate using lime addition at a mass application rate of 4/1(Ca/Al) at a temperature of 60°C. Furthermore, it was assumed that the aluminum concentration in etch was reduced by 80 percent, thereby reducing the quantity of aluminum in dragout from the etch tank. From data in Figures 8.2 and 8.4, the quantity of sludge produced during etch recovery was estimated to be 8.7 kg dry solids/kg aluminum removed. Based on these assumptions, sludge quantities were estimated for plant Al with and without an etch recovery system using lime addition and are presented in Table 8.3. The estimated quanity of wet sludge solids using conventional neutralization with an etch recovery system was 13.5 T/d. Conventional treatment without an etch recovery system would produce approximately 18.1 T/d, or 34 percent more wet sludge solids. Implementation of the etch recovery system using lime addition, therefore, would have a positive impact on sludge quantities.

Implementation of an etch recovery system would also result in significant chemical savings. Continuing with the use of plant Al as an example, the flow of spent etch was 6.3m^3/d as shown in Table 6.4. This flow, which was required to control the accumulation of aluminum (Al^{+3}) in the etch tank, would be eliminated, as would be the need for routine addition of virgin caustic. Using a cost for NaOH of $180/ton (1982), the chemical savings for virgin caustic would be approximately $500/d. The cost of lime would be approximately $100/d ($Ca(OH)_2$ at $38/ton (1982). The net savings in chemical costs would be approximately $400/d or $110,000/year. This savings in chemical costs would be offset initially by the capital and installation costs for a lime storage and dosing system, a dewatering system and associated hydraulic systems. The preliminary chemical cost data, however, indicate that the process is feasible and worthy of further consideration. Additional research is required before the process can be implemented.

Table 8.3 Sludge Quantities at Plant Al with and without Etch Recovery Using Lime Addition

Description	Aluminum Treated T/d	Sludge Solids: Solids Content Percent	Sludge Solids: Wet Sludge T/d
Conventional Neutralization			
All wastewaters	0.566	12	18.1
Conventional Neutralization with Etch Recovery System			
Conventional Neutralization of Rinsewaters	0.270	12	8.6
Spent Etch Recovery System (Lime Addition)	0.296	52.5	4.9
		TOTAL	13.5

Although the calcium aluminate sludge can easily be dewatered, the moisture in the sludge solids is caustic soda. This places the sludge in a hazardous category, requiring additional disposal costs over those typically required for conventional sludges. A perforate-basket centrifuge may, however, allow for a means of removing caustic soda associated with sludge solids with a water wash prior to disposal. This should be examined in detail. Additional information regarding process kinetics and stoichiorietry is required. In addition, information regarding utility of the recovered etch is critical to implementation of the process and must be finally established with further research.

Finally, the feasibility of the etch recovery process has been established herein. Additional laboratory-scale and pilot-scale testing is required to establish the full-scale utility of the process.

SECTION 9

RECLAMATION OF ALUMINUM-FINISHING SLUDGE AS LIQUID ALUM

INTRODUCTION

Sludges produced in the aluminum-finishing industry, especially in etching and anodizing plants, contain aluminum hydroxide as the primary chemical constituent. An overall objective of this project was to examine techniques which had the potential for elimination of sludge disposal problems through reclamation of sludge as useful products. Direct acidification of aluminum-finishing sludge with sulfuric acid to produce aluminum sulfate solutions was therefore investigated.

Published literature on recovery of aluminum sulfate from aluminum-finishing sludges is minimal. However, alum sludges from water treatment plants, have been used for the recovery of aluminum, as aluminum sulfate, for reuse as a coagulant. Since sludges from aluminum-finishing industries and alum sludges contain the same primary constituent, i.e., aluminum hydroxide (Saunders *et al*., 1982), it is possible that aluminum recovery technology used with alum sludges may also be applied to aluminum finishing sludges.

Recovery of Water Treatment Plant Sludges

Recovery of aluminum from alum sludges with sulfuric acid is a well known process. As early as 1903, aluminum recovery was practiced in the United States (Roberts and Roddy, 1960). Later, the process found widespread application in Japan, Great Britain and Poland (Chen *et al*., 1976).

Although some variations in the acid extraction process are encountered in practice, the process generally consists of a rapid-mix unit followed by a separator. Alum sludge is gravity thickened and underflow sludge is mixed with sulfuric acid in a rapid mix tank. Acidified sludge is transferred to a separator in which supernatant liquid is recovered for reuse as a coagulant in the water treatment process. Sludge from the underflow of the separator is neutralized with lime, dewatered and disposed to a lagoon or a landfill.

In the rapid-mix tank, reaction between sulfuric acid and aluminum-hydroxide sludge solids proceeds as follows:

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O \qquad (9.1)$$

As is apparent from the stoichiometric relationship, the amount of aluminum recovered varies with the quantity of acid added. Chen et al. (1976) observed that most alum sludge samples exhibited an acid demand which could be predicted from stoichiometric considerations for up to about 80 percent aluminum recovery. Beyond this level, acid demand could not be determined from stoichiometric relationships. When aluminum recovery was 80 percent effective, suspension pH was 3.0 for most of the sludge samples. Cornwell and Susan (1979) reported that aluminum recovery varied between 50 to 90 percent at pH 3 with five alum sludges. In addition, the optimal acid dose occurred at a sulfuric acid to total aluminum molar ratio of 1.5:1 which was approximately equal to the stoichiometric ratio. However, further increases in acid addition did not appear to increase aluminum recovery significantly. Experience at full-scale aluminum recovery plants in Japan indicated that 50 to 70 percent aluminum recovery at pH 2-2.5 was observed with alum sludges (Gruninger, 1975). Gruninger (1975) observed in pilot-plant studies that about 75 percent of influent aluminum hydroxide was recovered as alum at pH 2. However, Lindsey and Tongkasame (1975) reported 98 percent aluminum extraction at pH 2. Webster (1966) found that aluminum recovery was about 80 percent complete at pH 3.

With most alum sludges, complete aluminum recovery is possible. However, toxic metals and other contaminants are dissolved in the extraction process and may accumulate to undesirable levels with continued recycling of recovered alum. Webster (1966) and Isaac and Vahidi (1961), in addition, reported that supernatant coloration increased significantly at pH levels below pH 3. Isaac and Vahidi (1961) observed that the amount of color extracted from sludge had an adverse effect on the efficiency of recovered alum as a coagulant.

Wide variations observed in aluminum recovery may be due to differing sludge characteristics and experimental conditions employed. For example, Webster (1966) employed a slow-stirred settling unit with a detention time of 24 hours in place of a rapid-mix unit. Chen et al. (1976) used a mixing unit with a 30-minute detention time and stirring rate of 30 rpm. Cornwell and Susan (1979) applied a detention period of 15 minutes while Westerhoff and Daly (1974) reported the use of a 25-minute detention time for the acidulator in a pilot-plant study and 10 minutes in full-size plants in Japan. Goldman and Watson (1975) used a detention time of 10 minutes in an acidulator and Gruninger (1975) found that longer detention times contributed to high aluminum recoveries. There was also an indication that recovered alum concentration increased linearly with increasing solids concentration.

Detention times employed in practice for separators vary widely. The detention time employed by Chen et al. (1976) was one hour for settling tests conducted in a 1-litre graduated cylinder. Cornwell and Susan (1979) used a 1-litre graduated cylinder as a settling column and a 2-hour settling time. A volume reduction of approximately 80 percent was observed with three sludges (Cornwell and Susan, 1979). However, prior to acidification, sludge volume reductions of only 7 percent were achieved. In addition to sludge volume reduction, a reduction is achieved in the dry weight of residual solids. Isaac and Vahidi (1961) observed that the sludge volume could be reduced by 67 percent at pH 3 after a 24-hour settling period in a 250-ml graduated cylinder, and higher volume reductions were possible as lower pH values. However, in this case, coloration of supernatant occurred very rapidly. Goldman and Watson (1975) found that sludge volume could be reduced from 890 ml to 435 ml by lowering pH from 7.1 to 3.0 and employing a settling period of one hour in a 1-litre graduated cylinder. Westerhoff and Daly (1974) reported on the use of 14- to 20-hour detention times for the separator in pilot-plant studies. Detention times ranging from 14 to 60 hours did not influence the concentration of recovered alum. Finally, Webster (1966) used a detention period of five days in a separator.

Recovery of aluminum as an aluminum sulfate solution from water treatment plant sludges is practical, indicating the potential for application of alum recovery in the aluminum-finishing industry. It is therefore of benefit to examine current practices used in the industry for production of commercial-grade liquid alum.

Aluminum Sulfate Industry

The major user of aluminum sulfate is the pulp and paper industry where it is used in clarification of process waters, pH control of pulp slurries, setting of dyes and setting of size on pulp fibers. Other uses include coagulation of water and wastewaters, phosphorus removal from domestic and industrial wastewaters, production of fire extinguishers, treatment of white leathers, as an astringent in drugs and cosmetics, and as a mordant to fix dyes on textiles.

Production of commercial-grade aluminum sulfate equalled 1.05×10^6 metric tons and iron-free aluminum sulfate production equalled 1.3×10^5 metric tons in 1981 (U. S. Department of Commerce, 1982). The majority of the commercial-grade aluminum sulfate is produced by extraction of bauxite or clay with excess sulfuric acid at 100 to 120°C. The hot supersaturated suspension is clarified and mixed with water used to wash excess sludge solids to make liquid alum, while the clarified solution is concentrated by evaporation prior to formation of granular aluminum sulfate. Iron-free ($<$0.005 percent Fe_2O_3) aluminum sulfate is produced from acidification of alumina trihydrate ($Al_2O_3 \cdot 3H_2O$), due to the high level of iron typically present in bauxite and clays.

EXPERIMENTAL TECHNIQUES

Aluminum-Finishing Sludges

To evaluate the potential for reclamation of sludges produced in the aluminum-finishing industry as commercial-grade solutions of aluminum sulfate (i.e., liquid alum), sludge samples were obtained from numerous sources. The sludges examined included conventional anodizing sludges, sludges produced by segregated neutralization of spent etch and anodize acid, and etch-recovery sludge, as well as a bauxite sample.

Conventional Sludges--

Sludge samples from two anodizing plants were examined. Sludge samples were collected from plant A2 immediately following discharge from a rotary vacuum filter. Sludges at this plant were produced by conventional neutralization of rinsewaters during the week and by segregated neutralization of concentrated finishing waste on a weekend day. The sludge cake collected on the vacuum filter was therefore a mixture of the two sludge suspensions.

Sludge solids were also collected from plant A3 following dewatering on a plate-and-frame filter press. Conventional neutralization was utilized to treat all wastewaters, including spent etch and anodize acids, followed by gravity sedimentation. Sludge solids, in both instances, were transported to the laboratory in air-tight containers to prevent moisture losses.

Segregated Neutralization Sludge--

The potential for production of liquid alum from a sludge produced by segregated neutralization of spent caustic etch and anodize acid was examined using a sludge produced in the laboratory. Spent etch and anodize acid from plant A3 was used to produce a sludge cake using a neutralizaton temperature of 80°C and a neutralization pH of 8.5, in accord with procedures indicated in Section 7.

Etch Recovery Sludge--

The recovery of spent etch with lime addition (Section 8) produced a calcium aluminate sludge. However, due to high levels of calcium, this sludge was not amenable to the production of a commercial-grade liquid alum. Two proprietary processes for etch recovery have been presented by Fugi Sash Inc. and Alcoa, Inc. (Meyer et al., 1978; Brown, 1982) which result in production an aluminum-trihydrate sludge. To examine these materials, personnel at plant A2 collected representative samples of sludges from plants using the two processes and forwarded them to the laboratory in air-tight containers for investigation.

Bauxite--

To compare product quality and relative reactivity of aluminum-finishing sludges to that typical of the alum industry, a sample of bauxite from a local producer of aluminum sulfate was obtained. The material was collected immediately prior to acidification with sulfuric acid at the production site.

Experimental Reactor

Initial experimental investigations were conducted in covered, 2-litre, glass beakers which were mixed but not insulated or heated. Extractions made under these conditions were incomplete and unsatisfactory due primarily to the extensive heat loss from the low-volume and high-surface-area beaker. In conjunction with discussions with representatives from numerous producers of liquid alum, an alternative extraction system was devised which was consistent with that used in industry to evaluate the quality of bauxite, clay and other materials for production of liquid alum.

The reactor vessel was a 2-litre Pyrex beaker with a high-temperature plastic cover to minimize moisture loss during reaction. The reactor was mixed with a single-blade Teflon stirrer attached to a variable-speed motor. The reactor was placed on a hot plate during an extraction and heated to maintain a near-boiling temperature throughout a reaction period. Sulfuric acid addition was controlled using a 100-ml glass burette. Sample collection and acid addition were achieved through small holes in the cover on the reactor.

Experimental Procedures

To examine the potential for production of liquid alum from a sludge sample, the sludge was initially characterized. The solids content, both total and inert solids, of the sludge was determined at 103°C and 550°C. A 10- to 20-g sludge sample was dried at 103°C for 24 hours to determine total solids content and then combusted at 550°C for 30 minutes to determine the inert (or nonvolatile) solids content. Inert solids were determined since Saunders et al. (1982) determined that the composition of the inert solids was best approximated by the formula $Al(OH)_3$ for aluminum-finishing sludges.

Aluminum composition was determined on each sample. Sludges were repeatedly acidified to pH-2 with nitric acid and boiled until all solids were solubilized or the extraction was complete.

The next step in the extraction procedure required the determination of the quantity of sulfuric acid to be added. Using the inert suspended solids concentration as a measure of the $Al(OH)_3$ content of the sludge, acid requirements were estimated using Equation 9.1. A ten percent reduction in sulfuric acid was usually made to avoid formation of a product containing excess acid. In addition, the predicted final strength of the alum product was determined using Equation 9.1, in conjunction with the water content of the sludge determined in solids analyses. If the predicted strength of the product exceeded solubility limits, the quantity of water required to avoid supersaturation conditions was calculated.

To initiate an extraction, the complete reactor system was placed in a vented hood due to the potential for production of noxious gases during an extraction. Wet sludge samples were then placed in the reactor and acid addition was initiated. Due to the vigorous nature of the reaction, acid addition was restricted to flows of 10-15 ml/min. An excessive rate of acid addition resulted in production of extremely high reaction temperatures and production of excessive quantities of foam which would overflow the reactor. Slow addition of acid decreased the rate of foam production and minimized overflows.

Within five minutes of initiating the extraction with acid addition, stirring was initiated at 15 rpm. Initially, stirring was virtually impossible due to the thick gelatinous nature of sludge solids. Temperature of the extraction mixtures were maintained near boiling for the duration of the extraction using the heater plate.

Following acid addition and initial mixing of the extraction suspension, samples of 10-to 15-ml volume were collected and immediately filtered through a 0.45 μm glass-fiber filter. The filtrate was analyzed for free acid to determine the progress of the reaction. When free-acid content was less than 0.1%, the reaction was considered to be complete and the extraction was terminated. The contents of the reaction was then stored for further analysis.

EXPERIMENTAL RESULTS

The experimental investigation of direct acidification of aluminum-finishing sludges was focused on determination of process feasibility and on process requirements to assure production of a commercial-grade product. Several batch extractions were conducted on five sludge samples and a bauxite sample.

Sludge Characteristics

Five sludge samples were examined in the experimental studies. The two sludges from anodizing plants A2 and A3 were designated A2 and A3 herein. In addition, since the solids content for the sludge sample collected at plant A3 was relatively low, a portion of this sample was air-dried at a slightly elevated temperature to achieve a solids content near that of sample A2. The original sludge sample was designated A3-1 while the dried sample was designated A3-2.

Sludge produced in the laboratory by segregated neutralization of concentrated finishing wastes (see Section 8) was designated SN. The two etch recovery sludges were designated ER-1 and ER-2 with no distinction made to identify the source of the materials. Finally, bauxite was referred to as B.

Characteristics of the five sludge samples as used in the extractions are presented in Table 9.1. A2 sludge sample had a solids content of 21.3 percent, which was exceptional for anodizing plants. The solids content of A3-1 sludge was 13.5 percent and was typical of the solids contents achieved by the majority of the aluminum-finishing plants surveyed by The Aluminum Association, Inc. (Saunders _et al_., 1982). Drying of a portion of sample A3-1 produced a sample (A3-2) with a solids content near that of sample A2. The aluminum content, based on inert solids (IS) was 35.2 and 33.8 percent, respectively, for samples A2 and A3. These values were similar to the theoretical value for $Al(OH)_3$ of 34.6 percent and were typical of aluminum finishing sludges (Saunders _et al_., 1982).

As typical of segregated neutralization sludges (see Section 7), sludge sample SN had a high solids content, i.e., 32.9 percent. The aluminum content was the lowest of those examined, however, it was not significantly below that for aluminum-finishing sludges and was acceptable as a feedstock for production of liquid alum.

Table 9.1 Characteristics of Solids Extracted by Direct Acidification with Sulfuric Acid

	Dry Cake Solids		Aluminum Content
Sample	Total (percent)	Inert (percent)	(g/g IS*)
A2	21.3	16.8	0.352
A3-1	13.5	9.6	0.338
A3-2	21.1	15.5	0.338
SN	32.9	27.1	0.322
ER-1	95.1	94.2	0.373
ER-2	90.4	89.7	0.378
B	94.8	94.4	0.325

*IS = Inert Solids

Etch recovery sludge samples had extremely high solids contents of 90.4 and 95.4, indicating that the samples contained less than 10 percent moisture. These values were, in addition, in agreement with those presented by Brown (1982). Volatile materials accounted for approximately 1 percent of sludge solids, since inert solids ranged from 89.7 to 94.2 percent solids. The aluminum contents of the etch recovery solids ranged from 37.3 to 37.8 percent. These values were the highest of all those examined and indicated the potential for the presence of crystalline aluminum precipitates with decreased water contents and aluminum-oxide forms. This potential difference in chemical composition could affect aluminum extraction with acid addition and was investigated.

Finally, the bauxite sample was low in moisture and contained 32.5 percent aluminum. The results in Table 9.1 for aluminum content, however, do not reflect the nonreactive portion of bauxite. Approximately 40 percent of the inert solids were refractory and could not be extracted. The value for aluminum of 32.5 percent is based on the reactive portion of the inert solids alone. The aluminum content was approximately 19.5 percent, when based on total inert solids.

In general, aluminum-finishing sludges contained high levels of aluminum relative to bauxite and appeared to be excellent feedstocks for production of liquid alum. The relatively high moisture contents for anodizing sludges, however, indicated potential for dilution of the final product below acceptable levels.

Chemical Balance for Alum Extractions

In initiating acid extractions of sludge samples, the primary objective was to produce a liquid alum with the highest strength possible without exceeding saturation concentrations at ambient temperatures. Commercial-grade liquid alum typically contains aluminum at concentrations of 7.5 to 8.5 percent as Al_2O_3 (i.e., 43.7 to 49.5 percent as $Al_2(SO_4)_3 \cdot 14H_2O$). To establish stringent requirements for liquid alum produced from aluminum-finishing sludge, initial estimated concentrations of 8.2 to 8.5 percent as Al_2O_3 were established to determine chemical quantities for extraction experiments. However, if water contained in sludge samples would not allow for production of this concentration, then the maximum possible concentration was used in the extractions. Using Equation 9.1 and including the moisture contained in the wet sludge samples, chemical requirements for extraction experiments were established. Bauxite was extracted using a higher relative acid concentration due primarily to the refractory nature of these solids.

Based on the above estimating procedures, the chemical and sludge additives used in the extractions are presented in Table 9.2. All anodize and segregated neutralization sludges were extracted at 8.2-8.3 percent Al_2O_3 except sample A3-1. Due to the low solids content of this sludge, i.e., 13.5 percent solids, sludge moisture diluted the extraction mixture and an estimated maximum of 5.3 percent Al_2O_3 was achievable. The high solids contents of the SN sample, on the contrary, resulted in an additional requirement for water, i.e., 0.56g/g of wet sludge solids, or 277g. Etch recovery sludge samples were easily extracted using estimated Al_2O_3 concentrations of 8.3 and 11.0 percent. This was achieved by either adding the required dilution before or after conducting the extraction. In both cases, however, the estimated final Al_2O_3 concentration was 8.3 percent and water was added at the rate of 2.1-2.3g H_2O/g wet sludge. Bauxite was extracted at a high acid concentration but water was added at the rate of 4.6g H_2O/g bauxite following extraction to reduce the strength of the liquid alum solution from 14 to 8.3 percent as Al_2O_3.

Sludge Extraction by Direct Acidification

Batch alum extractions were conducted and samples were taken periodically to determine the extent of reaction using free-acid measurements. In addition, samples were collected periodically to monitor the reaction for all samples except bauxite. Bauxite samples were extremely viscous and could not be filtered within a reasonable time period to monitor the extraction reaction. Filtrate samples were not collected for samples ER-1(B) and ER-2(B) due to the supersaturated conditions under which these experiments were conducted.

Table 9.2 Chemical Additives in Alum Extractions

		Extraction Additives				
Sample	Estimated Al_2O_3 (percent)	H_2SO_4 (g)	Inert Sludge Solids (g)	Sludge Water (g)	Dilution Water (g)	Post-Extraction Dilution Water (g)
A2	8.3	317	168	832	0	0
A3-1	5.3	181	96	904	0	0
A3-2	8.2	285	151	804	0	0
SN	8.3	243	129	369	277	0
ER-1(A)	8.3	242	106	6	665	0
ER-1(B)	11.0	242	106	6	411	254*
ER-2(A)	8.3	256	112	12	695	0
ER-2(B)	11.0	256	112	12	432	263*
B	14.0	144	83	5	160	406*

*Dilution water added after extraction to achieve final Al_2O_3 concentrations of 8.3 percent.

Filtrate aluminum concentrations for several samples are presented in Figure 9.1. A liquid alum concentration of 8.3 to 8.5 percent as Al_2O_3 is reflective of saturation conditions and maximum practical concentrations for liquid alum. Therefore, within approximately a 40-minute period, aluminum concentrations for samples A2, A3-2, and SN were at saturation levels. Extraction of samples ER-1(A) and ER-2(A) were virtually identical and are presented in Figure 9.1 with an ER designation. The solids in the etch recovery sludges were more difficult to extract since a 120-minute period was required to reach aluminum concentrations above 7.5 percent as Al_2O_3. Data for extraction of sample A3-2 followed the same trend as sample A3-1 with the exception that the maximum aluminum concentration was 5.8 percent as Al_2O_3. Data could not be collected for the bauxite sample but the extraction was not complete until after three hours at an elevated acid concentration.

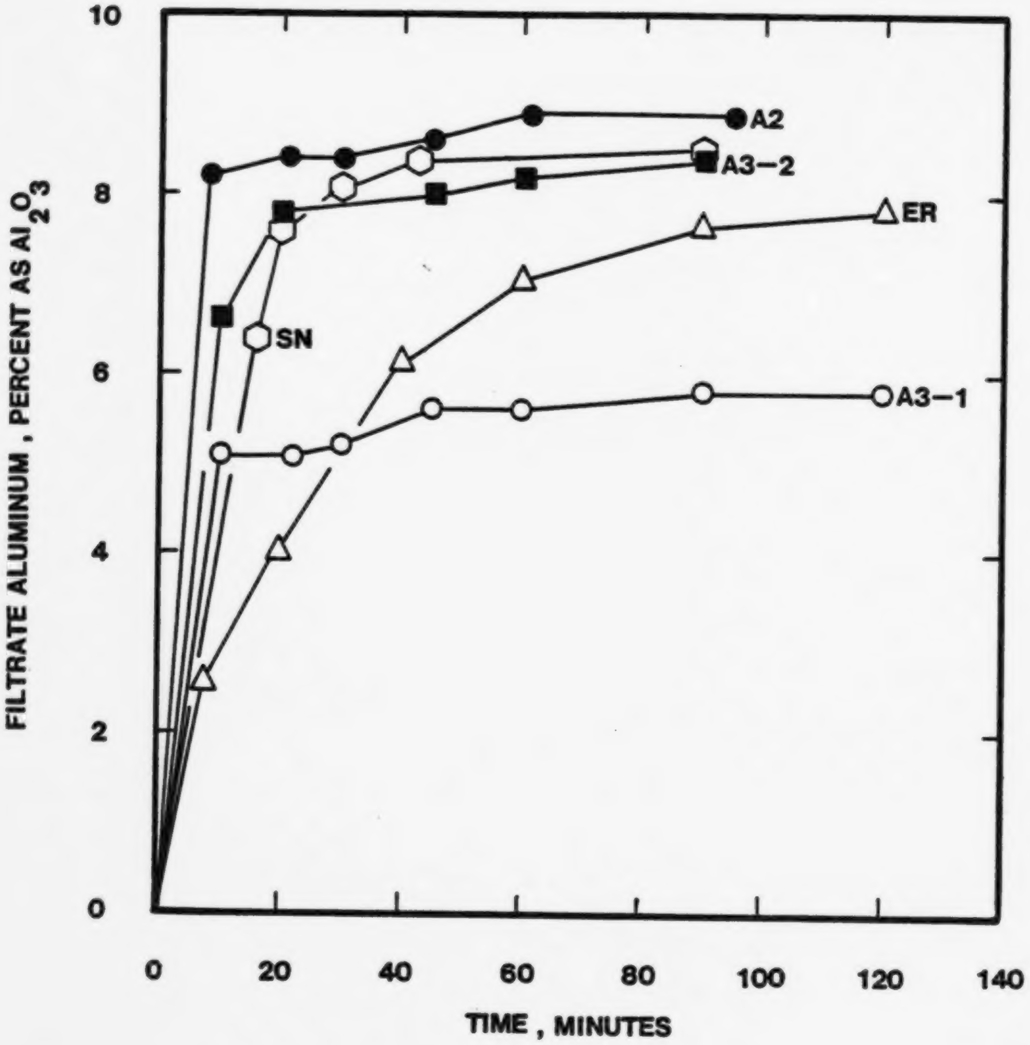

Figure 9.1 Filtrate Aluminum Concentrations in Direct-Acidification of Aluminum-Finishing Sludges.

Therefore, sludge samples from aluminum-finishing plants were readily extractable using stoichiometric addition of sulfuric acid within a two-hour period. The sludge samples were, in addition, more easily extracted than bauxite, the common feedstock for alum production.

With respect to quality of the final product, data for Al_2O_3, free acid and free Al are presented in Table 9.3. The estimated Al_2O_3 concentrations in Table 9.3 were those presented in Table 9.2 (following post-extraction dilution). With the exception of ER-1(A) and ER-2(A), measured Al_2O_3 concentrations exceeded estimated values by 0.1 to 0.6 percent, indicating excellent product quality. In addition, with exception of A3-1, the Al_2O_3 concentrations were within or slightly above the typical range of values for commercial-grade liquid alum (i.e., 7.5 to 8.5 percent as Al_2O_3). Samples ER-1(A) and ER-2(A) were extracted at estimated Al_2O_3 concentrations of 8.3 percent. As indicated in Figure 9.1, the extraction was not as rapid for these samples as it was for other aluminum-finishing sludges. However, when dilution water was added after completion of the extraction with samples ER-1(B) and ER-2(B), and not at the beginning, the higher acid concentration accelerated the extraction of aluminum and Al_2O_3 concentrations of 8.5-8.7 percent were achieved. This option of post-extraction dilution is obviously one which could be practiced in prototype systems, thereby indicating excellent potential for use of etch recovery solids for alum production.

Sample A3-1 was extracted to a concentration of 5.8 percent Al_2O_3 which was below acceptable levels for full-strenth liquid alum. The initial solids content of this sample was too low to allow for production of a commercial-grade material. From data for samples A2 and A3-1, it would appear that a solids content of approximately 21 percent is required to be able to achieve commercial-grade levels. The values of free Al included in Table 9.3 are indicative of slightly saturated conditions. This could be corrected by the addition of water to the extraction mixture and may have, in fact, been caused by the loss of moisture during the extraction period.

Due to the predominant use of liquid alum by the pulp and paper industry, the principle concern with respect to alum quality is not for toxic metals, for example, but for constituents which result in poor product quality. These contaminants of concern industrially include iron (Fe), potassium (K), calcium (Ca), magnesium (Mg), titanium (Ti), ammonia (NH_4) as well as total heavy metals. Analyses of aluminum-finishing sludges indicated that ammonia and total heavy metals were not of major concern (Saunders et al., 1982). However, analyses for Fe, Ca, K, and Mg were warranted. Concentrations of these metals in liquid alum solutions are presented in Table 9.4. All of the alum samples produced in the study were within typical industrial limits as extracted from numerous industrial sources (Note: there are no fixed limits which are enforced by a regulatory or industrial-users group). The products therefore met specifications on aluminum content and on the major contaminant cations and should be of acceptable industrial quality. In addition, the etch recovery sludges were below the limit set for iron-free liquid alum, i.e., 35 mg/l as Fe.

Table 9.3 Composition of Extracted Liquid Alum Products

Sample	Al_2O_3 (percent) Estimated	Al_2O_3 (percent) Measured	Free Acid (percent)	Free Al (percent)
A2	8.3	8.9	--	0.62
A3-1	5.3	5.8	--	0.52
A3-2	8.2	8.4	--	0.61
SN	8.3	8.5	--	0.37
ER-1(A)	8.3	7.6	0.38	--
ER-1(B)	8.3	8.7	--	0.67
ER-2(A)	8.3	7.9	0.26	--
ER-2(B)	8.3	8.5	--	0.42
B	8.3	8.4	--	0.04

Table 9.4 Trace Metal Composition of Liquid Alum

Sample	Fe mg/l	Ca mg/l	K mg/l	Mg mg/l
A2	543	22	16	102
A3-1	1135	166	11	401
A3-2	1923	278	15	670
SN	233	10	44	252
ER-1	30	<1	<1	54
ER-2	28	<1	<1	31
B	822	40	23	2
Typical Industrial Standard	<2100	<300	<125	<800

Since iron-free liquid alum is sold for about twice the price of commercial-grade liquid alum, implementation of etch recovery systems at anodizing plants may result in production of sludges which could be used to produce an alum product of higher commercial value.

DISCUSSION

To examine the potential for reclamation of aluminum-finishing sludges by direct acidification, data presented by Saunders *et al*. (1982) for numerous anodizing and etching sludges were examined.

Sludge Reclamation by Direct Acidification

Dry inert solids in aluminum-finishing sludges contain approximately 35 percent aluminum and are best represented by the formula $Al(OH)_3$. The reaction associated with the addition of sulfuric acid to wet aluminum-finishing sludge solids is therefore represented by:

$$Al(OH)_3 + X\ H_2O + 1.5\ H_2SO_4 \rightarrow 0.5\ Al_2(SO_4)_3 + (3 + X)\ H_2O \qquad (9.2)$$

where X is indicative of the molar quantity of water associated with wet sludge solids. Sulfuric acid requirements therefore are equal to 1.8 kg/kg dry inert sludge solids and alum production rates are equal to 2.4 kg $Al_2(SO_4)_3$/kg dry inert sludge solids or 0.72 kg Al_2O_3/kg dry inert sludge solids. The composition of commercial-grade liquid alum is approximately 8.3 percent as Al_2O_3, or 27 percent as $Al_2(SO_4)_3$. Using these latter values in Equation 9.2, a sludge containing 16.8 percent $Al(OH)_3$ is required as a minimum to produce an acceptable commercial-grade liquid alum. However, since aluminum-finishing sludges contain approximately 70 to 80 percent inert solids (Saunders, *et al*., 1982), a more realistic estimate for minimum solids concentrations is between 21 and 24 percent dry-solids (measured at 105°C).

Data presented in Tables 9.1 and 9.3 for sludge samples A2 and A3-2 indicated that commercial-grade alum could be produced with sludges containing inert solids of 16.8 and 15.5 percent, respectively, and total solids of 21.3 and 21.1 percent, respectively. These measured values, in conjunction with estimated values above, strongly indicate that sludge solids concentrations in excess of 21 percent are required to effectively produce liquid alum with a conventional aluminum finishing sludge. The quantity of water associated with sludges at lower solids contents result in dilution of the product, as indicated by results with sample A3-1. Data from a study conducted by The Aluminum Association Inc. (Saunders *et al*., 1982) indicated that conventional sludges following dewatering had solids contents ranging from 7.4 to 20 percent and laboratory data presented by Saunders *et al*. (1982) indicated a range of 8.5 to 20.1 percent solids. These data therefore strongly indicate that reclamation of aluminum-finishing sludge can only be achieved if sludge moisture content of conventional sludges is reduced.

Data presented for sludge solids produced by segregated neutralization and by recovery of spent etch as an aluminum trihydrate indicated they were excellent sources for production of liquid alum. The moisture content of these sludges, in addition, required that water be added to produce a commercial-grade liquid alum. Finally, segregated neutralization and etch recovery processes are both focused on treatment of the major source of waste aluminum at finishing plants, i.e., spent etch, and have excellent potential for application in conventional aluminum-finishing plants. Implementation of either process would therefore result in significant sludge volume reduction as well as enhance the potential for production of liquid alum using a mixture of segregated-neutralization or etch-recovery sludge and conventional aluminum-finishing sludge. In addition, utilization of an etch recovery system has potential for production of an iron-free liquid alum which has a high market value.

Engineering Significance

Recovery of aluminum-finishing sludges as commercial-grade liquid alum will typically require alterations in existing treatment systems to minimize sludge moisture content and an additional reactor system to produce liquid alum by direct acidification. Alterations in existing technology vary from relatively minor changes, such as improving performance of existing dewatering systems and addition of a segregated-neutralization system, to such major changes as installation of an etch recovery system. These changes, however, are plant-specific and encompass numerous other advantages, including chemical saving, and changes in finishing techniques. Therefore, to evaluate the engineering significance of an alum production system to reclaim sludge solids, the analysis is to be conducted with the assumption that the subject sludge is amenable to reclamation, i.e., it has a solids content greater than 21 percent.

To examine the viability of alum production, it is necessary to determine the quantity to be produced and the cost of production. For a plant with an aluminum production rate of 500 ton/month, approximately 2 to 4 percent of aluminum production, or 10 to 20 ton/month, will be discharged to wastewater treatment resulting in the production of approximately 29 to 58 ton/month of dry inert sludge solids (Section 6 and Saunders et al. (1982)). In accord with Equation 9.2, direct acidification would result in the production of approximately 70 to 140 ton/month of $Al_2(SO_4)_3$. Since liquid alum is typically shipped in tank-truck quantities of 4000 gallons, or 22 tons of 8.3 percent (as Al_2O_3) liquid alum, approximately 11 to 22 tank-truck loads of liquid alum would be shipped on a monthly basis.

With respect to the costs of production, chemical costs are easily evaluated on a tank-truck load basis. The production of a load of liquid alum requires the addition of 5.3 ton of H_2SO_4 to approximately 3.9 ton of dry sludge solids. Current costs of sulfuric acid range from \$57 to \$85/ton (virgin 100% H_2SO_4) while current costs of liquid alum range from \$130-\$135/ton (as 17 percent Al_2O_4) (Chemical Marketing Reporter, 1982). Therefore, the chemical cost to produce a load of liquid alum is \$300-\$450 while the market value of the alum is approximately $1,400. However, due to the relatively small volume of liquid alum produced at a plant, it is most probable that the liquid alum will be marketed through a chemical supplier and liquid alum would probably be sold at a lower rate than current market value. Therefore, assuming a value of $80/ton for liquid alum (i.e., 60 percent of market value), the purchase price of a tank-truck load of liquid alum would be reduced to $850. The net payback would be from $350 to $550 for each load of liquid alum. For a plant with a metal-production capacity of 500 ton/month, the revenue generated by producing and selling liquid alum would range from $3,850/month to $12,100/month ($46,200 to $145,200/year). This range of values includes variations in aluminum losses during aluminum finishing as well as variations in chemical costs. Alum production from aluminum sludges is therefore favorable with respect to chemical costs.

Implementation of a sludge reclamation system will require that existing sludge treatment systems remain in operation and that a dewatered sludge with a minumum of 21 percent solids be produced. To evaluate the overall viability of a reclamation system herein, it is assumed that an existing system can meet the minimum solids content requirement.

A schematic diagram of an alum reclamation system is presented in Figure 9.2. The components of the system include: (i) an acid-storage facility; (ii) a sludge conveyor from a sludge dewatering system to the reclamation facility; (iii) a reaction vessel with stirrer; (iv) multiple alum-storage tanks; (v) an alum transfer facility to load alum onto tanker cars and (vi) a piping-pump network to transfer alum from the reaction to storage tanks and the transfer facility. To evaluate the capital costs associated with such a facility, it is assumed that an average of 11 tank-truck loads of liquid alum are to be produce monthly or that an average of 29 tons/month of dry inert sludge solids are to be treated. The capacity and descriptions of the reactor systems required for such an alum production facility are presented in Table 9.5 and the estimated costs associated with construction of the facility are presented in Table 9.6. The total cost of $80,000 is a conservative estimate which could be lowered considerably when existing storage facilities, site construction and plant engineering capabilities are considered. Since existing sludge disposal facilities and services will be virtually eliminated (except for small fractions of bottom residuals) and, more importantly, since personnel associated with sludge transport and disposal will not be required, no additional operational staff will be required upon installatin of the sludge reclamation system.

The overall economic assessment for a sludge reclamation system indicated that equipment costs would be $80,000 while the net payback for chemicals is $46,200 to $72,600/year for a plant producing 11 tank-truck loads of liquid alum on a monthly basis. Therefore, a sludge reclamation facility could be installed at a treatment plant with a pay-back period of approximately 14 to 21 months. This range is based on conservative figures for equipment and net

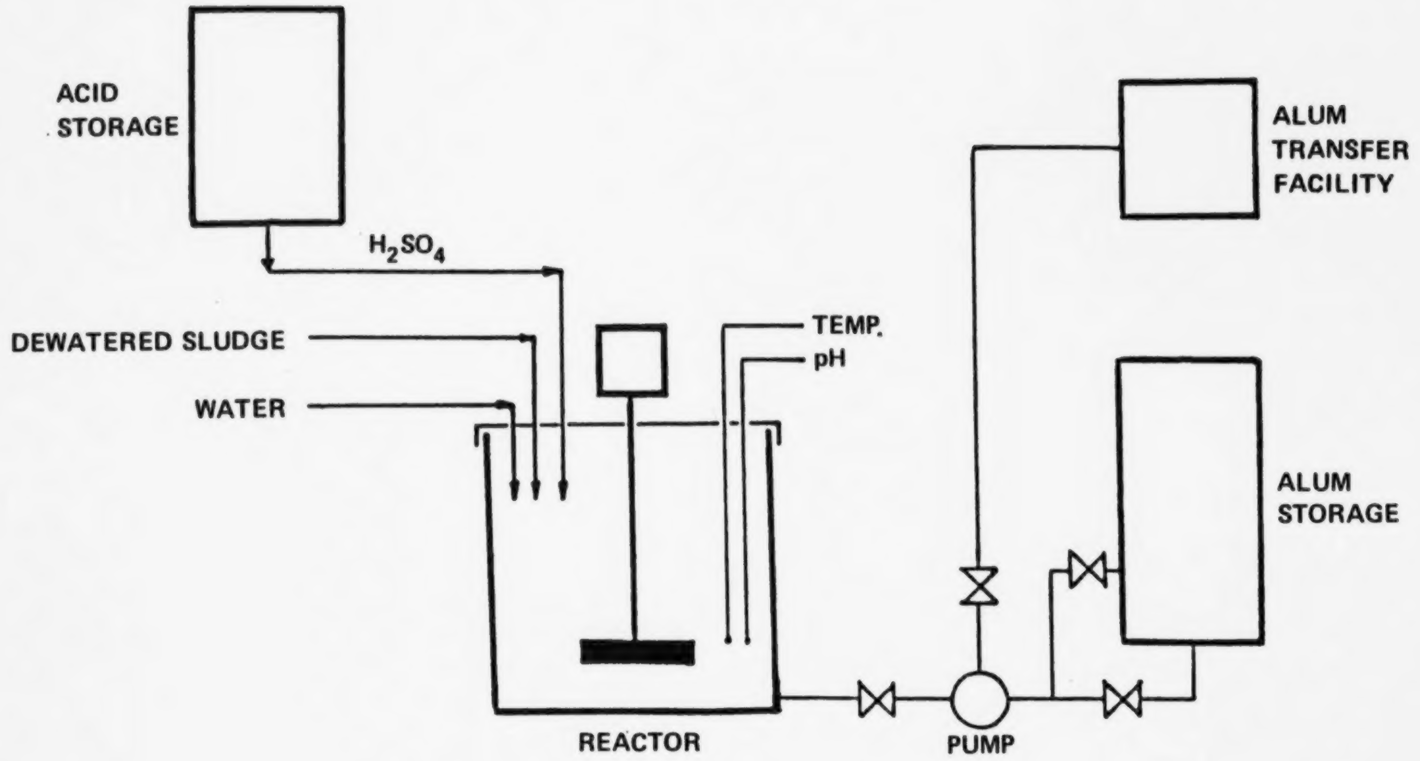
ACID STORAGE
H_2SO_4
DEWATERED SLUDGE
WATER
TEMP.
pH
REACTOR
PUMP
ALUM TRANSFER FACILITY
ALUM STORAGE

Figure 9.2 Schematic Diagram of an Alum Production Facility

Table 9.5 Description of Equipment Required for an Alum Reclamation Facility

Component	Volume (m^3)	Description
Acid-Storage Tank	15	Lined fiberglass or CPVC.
Reactor Tanks (2)	15	Insulated and lined fiberglass or CPVC; 2-10 HP mixer and pH and temperature probes required; pump to remove solution from reactor required.
Alum-Storage Tanks (2)	40	Lined fiberglass or CPVC.
Transfer Facility	--	Platform with flexible connectors required to fill tank car.

Table 9.6 Equipment Costs for an Alum Reclamation Facility

Item	Costs
Equipment	
i. Acid Storage, Reactor and Alum Storage Tanks	$30,000
ii. Sludge Conveyor; pH and Temperature Monitors; Stirrer and Reactor Control System; Pump, Valves and Piping	3,000
Engineering	
i. Site preparation, concrete pad and supporting facilities	10,000
ii. Reactor installation and electrical services	10,000
iii. Engineering preparation; Plant start-up and operation	27,000
3. TOTAL	$80,000

chemical revenues indicating a potential for a shorter pay-back period. In addition to the direct economic potential, sludge reclamation would also eliminate the need for expansion of sludge disposal facilities and allow for gainful development of present disposal sites. It would also minimize future environmental concerns associated with long-term storage/disposal of sludge in a land disposal facility. It is apparent that the reclamation of aluminum-bearing sludges produced at aluminum finishing plants (e.g., etching and anodizing plants) is practical and is worthy of further investigation by the industry.

SECTION 10

ENGINEERING SIGNIFICANCE AND APPLICATIONS

The research presented on characterization, treatment, reclamation and disposal of aluminum-finishing wastewaters in this and an initial project report provide a basis for improving waste treatment practices in small, medium and large industrial plants in which aluminum is finished. Improvements can include minor changes in conventional treatment practices or incorporation of numerous innovative treatment systems to significantly reduce or eliminate sludge disposal problems. Since the research has been conducted using actual wastewaters, sludges and finishing solutions from five etching, anodizing and painting plants in the United States, the results are directly applicable to wastewater treatment systems in many aluminum-finishing plants. The results, however, are based on laboratory investigations of wastewater treatment systems. While much of the information is conclusive enough to warrant development of full-scale systems, without exception, pilot-scale investigation of many of the comprehensive treatment systems is warranted to determine the ultimate impact on the finishing of the aluminum product as well as the success of the waste treatment process.

CONVENTIONAL TREATMENT SYSTEMS

In etching and anodizing plants, spent caustic etch and dragout from caustic etch tanks are the major sources of waste aluminum while rinsewaters are the major sources of wastewater. Implementation of water conservation practices and repeated use of rinsewaters in counter-current rinse systems will serve to reduce wastewater discharges. However, the major problem in treatment of aluminum-finishing wastes is the disposal of thickened or dewatered sludge solids. Surveys of two plants in the study indicated that wet dewatered-sludge quantities were potentially equal to 33 to 90 percent of the mass of finished aluminum product. Reduction in or reclamation of this quantity of sludge is therefore the major waste treatment task facing the industry.

Results presented in an earlier report (Saunders et al., 1982) indicated priority-pollutant metals were present in conventional aluminum finishing sludges at relatively low levels but were not readily extracted from dewatered sludges, even in the aggressive environment typical of sanitary landfills. Issues of sludge toxicity are, therefore, minor and the major issue is associated with the gelatinous, voluminous nature of aluminum hydroxide suspensions produced upon conventional neutralization of aluminum-finishing wastewaters.

Conventional treatment of the majority of aluminum-finishing wastewaters includes multi-stage neutralization of rinsewaters using spent etch and acids to adjust suspension pH to near-neutral values. Clarification in a gravity sedimentation basin follows neutralization with the clarified effluent being discharged to a receiving stream or municipal sewer for further treatment. Thickened underflow sludge is discharged to lagoon systems or dewatered with mechanical systems or gravity-drainage beds prior to land disposal. This latter step of sludge treatment and disposal is the area where major improvements are required.

Improvements in clarification characteristics of conventional wastewater suspensions is possible with use of polyelectrolyte addition. Results are so dramatic that polyelectrolyte use is all but required to effectively clarify these wastewaters (Saunders et al., 1982). Polyelectrolyte conditioning, in addition, results in significant improvements in sludge thickening properties. The improvements in thickening properties are among the most dramatic which can be achieved in conventional treatment systems. Field observations at industrial plants indicate that controlled addition of polyelectrolytes is not commonly achieved and that many waste treatment problems probably result from lack of this control. Precise monitoring and control of polyelectrolyte addition should be practiced.

With respect to dewatering, polyelectrolyte addition resulted in major improvements in rates at which water could be removed from thickened sludges. However, reduction in sludge moisture content could not be achieved and no reduction in wet sludge volume was possible.

Techniques for major improvements in conventional treatment systems beyond use of polyelectrolyte conditioning are not available. Refinements in current operational procedures should be pursued but present treatment practices are commonly within limits of current state-of-the-art technology. Major innovative changes in waste treatment practices are required.

INNOVATIVE TREATMENT SYSTEMS

In-depth industrial surveys at plant A1 and A3 indicated that waste sludge solids were attributable to aluminum removal from the surfaces of alloys finished. Reduction in waste sludge solids are therefore only possible with changes in the finishing process utilized in the industry. In addition, the quantities of wastes produced in painting lines were approximately 50-fold less than those from anodizing lines. Chromium in dragout from finishing solutions and aluminum removed from alloy surfaces were the major contaminants in paint-line wastes. Again, changes in the finishing process are required to further reduce this minor source of sludge solids.

Investigation of new techniques to be used in altering aluminum-finishing processes was well beyond the scope of this project. Therefore, emphasis was placed on investigation of innovative processes which had potential for reduction in the volume of sludge solids produced and reclamation of sludge solids as a product for reuse.

Sludge Volume Reduction

Moisture contents of conventional aluminum finishing sludges are typically equal to or greater than 80 percent. Reduction in sludge moisture content is therefore an obvious way in which sludge volume, and therefore sludge mass, can be reduced. Although not examined herein due to the lack of a pilot-scale system, filter presses typically produce sludges with lower moisture contents than other mechanical systems and should be examined for treatment of aluminum-finishing wastes. An alternative technique to reducing sludge moisture content was to alter the chemical composition of the sludge solids and avoid formation of amorphous, gelatinous aluminum-hydroxide solids. To achieve this objective, waste sources had to be isolated to provide for control over the conditions of chemical precipitation.

The major source of waste aluminum was shown to be spent caustic etch suspensions and isolation of this waste source is easily achieved. To produce a crystalline precipitate as opposed to an amorphous one, two innovative processes were investigated.

Removal of aluminum from spent etch was possible using lime addition to heated solutions of caustic etch. A calcium aluminate suspension was formed which could easily be dewatered to solids contents of 48 to 52 percent. This alteration in the form of the aluminum precipitate resulted in reduction in sludge volume through reduced moisture content of the dewatered sludge. In addition, the process provided for the additional economic benefit of recovery of the caustic etch solution. Waste reclamation is, therefore, possible as is the concurrent reduction in sludge volume.

Application of etch recovery with lime addition may be most effectively applied in small finishing plants where relatively small quantities of waste do not allow for application of capital-intensive recovery systems, but disposal costs are prohibitive. Installation of a small heated reaction vessel and a mechanical dewatering system (e.g., perforate basket centrifuge, filter press or vacuum filter) would provide for recovery of all spent etch while producing a low-volume sludge for disposal. Reduced disposal costs for spent etch as well as chemical saving for make-up caustic soda could prove to make the process cost-effective. These benefits are, furthermore, not to be limited to small-scale systems but could prove to be extremely beneficial, especially if sludge solids could be collected without being saturated with spent etch using a system to wash the dewatered sludge, e.g., perforate-basket centrifuge with a water-spray.

A second process investigated to alter the chemical characteristics of aluminum precipitates and thereby reduce sludge volume was segregated neutralization of concentrated finishing wastes. Spent caustic etch and anodize-acid regenerant are major sources of waste aluminum and are, respectively, highly alkaline and acidic. Controlled neutralization of these concentrated wastes at alkaline pH values produced dewatered suspensions which had solids contents of from 33 to 53 percent. The solids produced were similar to crystalline forms, e.g., gibbsite, bayerite, and pseudo-boehmite, and had improved sludge handling properties. This option also allowed for treatment of approximately 70 to 80 percent of the total waste metal in a small volume of wastewater using a small neutralization system. Furthermore, data collected following a 24-hour period of aging at ambient temperature and those obtained from plant A2 regarding segregated neutralization indicated that the improved handling properties of these solids were not altered with time or upon mixing with conventional, amorphous sludge suspensions. Therefore, segregated neutralization should have potential for application at all aluminum-finishing plants in which concentrated alkaline and acidic finishing wastes can be isolated for segregated treatment. Discharge of concentrated suspensions following segregated neutralization to a conventional neutralization system or clarifier influent or mixed with thickened conventional sludge solids should improve the ultimate solids content achieved following dewatering and thereby reduce sludge volume.

Reclamation of Aluminum-Finishing Wastes

Finishing of extruded aluminum results in the loss of from 2 to 5 percent of the aluminum to rinsewaters and finishing solutions. Recovery of the waste metal or contaminated finishing solutions would reduce overall finishing costs and minimize waste treatment and disposal problems. Two innovative processes were examined in this regard.

Treatment of spent etch with lime results in precipitation of aluminum as a calcium aluminate which can be removed by direct filtration of the suspension. Complete removal of aluminum is possible and is controlled by reaction time, temperature and quantity of lime added. Following filtration, the filtrate etch solution can be returned to a process etch tank. Caustic soda addition would be reduced to that equal to dragout and that contained in calcium-aluminate sludge solids. This reclamation process has application in all metal-finishing operations especially those in which neutralized wastewaters are discharged to a municipal sewer. This would allow for separate treatment of a suspension which is difficult to discharge and recovery of the spent etch.

The innovative process which has potential for elimination of all aluminum-finishing waste solids and recovery of waste aluminum as a marketable product is direct acidification to produce liquid alum (i.e., an aluminum sulfate solution). Sludges produced by conventional and segregated neutralization were extracted with sulfuric acid to form commercial-grade liquid alum with a quality equal to that formed commercially from bauxite. In addition, sludges produced with the Fugi Sash and Alcoa etch-recovery systems were excellent feedstocks for production of liquid alum.

Implementation of a system to reclaim waste-aluminum was shown to be contingent upon production of a dewatered sludge suspension with a solids content of approximately 21 percent or higher. Conventional treatment systems do not routinely result in production of such a dewatered sludge and one of numerous techniques must be employed to reduce sludge moisture content. Options include, for example, segregated neutralization of concentrated finishing solutions and installation of an etch recovery system producing an aluminum-trihydrate sludge. With such systems, all waste aluminum can be converted into a commercially marketable product.

Implementation of such a reclamation system, therefore, requires installation of a system to increase sludge solids content and a sludge extraction and alum storage system. Chemical composition data indicate that chemical quality of the liquid alum solutions produced were of acceptable quality. However, variations in sludge quality and composition could affect product quality as well as product clarity. Finally, pilot-scale verification of laboratory results must be pursued before it is to be implemented in full-scale systems. Major issues as yet unresolved include heat requirements during extraction, clarity of extracted suspensions and procedures required to assure acceptable clarity, and control systems required to operate the extraction system.

SECTION 11

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